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Time evolution of the thermodynamic temperature scale

Andrea Peruzzi

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Outline

Reflection on the historical development of:

- The concept of temperature
- Its measurement scales

➢ Part 1:

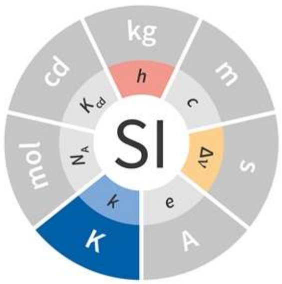
- Main milestones in the path to our current understanding of the thermodynamic temperature and its measurement scale
- Basic concepts of *measurement theory*

➢ Part 2:

- Evolution of the thermodynamic temperature scale over the past 100 years

➢ Conclusions

The definition of thermodynamic temperature



- BIPM website:
  - SI unit of thermodynamic temperature
    - How SI unit is defined:
      "*by taking the fixed numerical value of k to be* 1.380649·10^{-23} JK^{-1}"
    - How SI unit is realized
      → *Mise en pratique*

The definition of thermodynamic temperature

- How is thermodynamic temperature defined?
  - Phenomenological approach (Kelvin, 1854):
    - Principles of classical thermodynamics $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$
  - Axiomatic approach (Caratheodory, 1909):
    - Mathematical theorem on differential forms
    - Demonstrates the existence of temperature as an integrating factor $\tau(x, y, z)$ for $đQ$

$$\frac{đQ}{\tau} = dS$$

  - Microscopic approaches:
    - Kinetic theory of gases $E_{\mathrm{Kin}} = \left(\frac{3}{2}\right) kT$
    - **Statistical mechanics** $P(E)dE = \Omega(E) exp\left(-\frac{E}{kT}\right)$
    - Quantum mechanics $P(E)dE = \frac{1}{exp\left(\frac{E-\mu}{kT}\right) \pm 1}$

Part 1

Major milestones that led to the modern definition of thermodynamic temperature

Thermal equilibrium and zeroth principle

- **Thermal equilibrium:**
  two thermodynamic systems A and B are in thermal equilibrium if:
  when they are brought into mutual thermal contact,
  they continue to be in the states in which they were prior to the establishment of thermal contact

- **Zeroth Principle:**
  if A is in thermal equilibrium with C and
  B is in thermal equilibrium with C,
  then A and B are in thermal equilibrium with each other

Thermal equilibrium and zeroth principle

- Provide a procedure to determine equality of temperatures:
  two systems *A* and *B* have the same temperature if they are in thermal equilibrium (when they are brought into mutual thermal contact…)
  - Given any two systems *A* and *B*, you can determine whether $t_A = t_B$ or $t_A \neq t_B$

Measurement theory (Stevens, 1946)

- We can already create a 1st simple type of measurement scale
- **Nominal scale**: can establish equality
  - Example: numbers on the uniforms of football players
    - Numbers are used as names, the actual number has no meaning (number 10 is not two times better than number 5)

2^{nd} principle of thermodynamics

- Provides a procedure to order temperatures
- We can label each temperature with a serial number but we cannot assign a value to it:
- Hotness series: $\{h\} = \{h_1, h_2, h_3, \ldots h_k, \ldots\}$

Measurement theory

- We can create a 2^{nd} (more interesting) type of measurement scale
- **Ordinal scale**: can establish equality and order
  - Not only $h_i = h_j$ or $h_i \neq h_j$
  - But also: $h_i > h_j$ or $h_i < h_j$

Empirical temperature scales

- Empirical temperature scale:

  any order-preserving one-to-one mapping of the hotness series:

  $t : h \rightarrow \mathbb{Q}$

$$\begin{array}{cccccc} h_1 & h_2 & h_3 & \ldots & h_k & \ldots \\ \downarrow & \downarrow & \downarrow & & \downarrow & \\ t_1 & t_2 & t_3 & \ldots & t_k & \ldots \end{array}$$

- Non-uniqueness of empirical temperature scale:

  if t is an empirical temperature scale, then
  any monotonic function $f(t)$ is also an empirical temperature scale

Measurement theory:

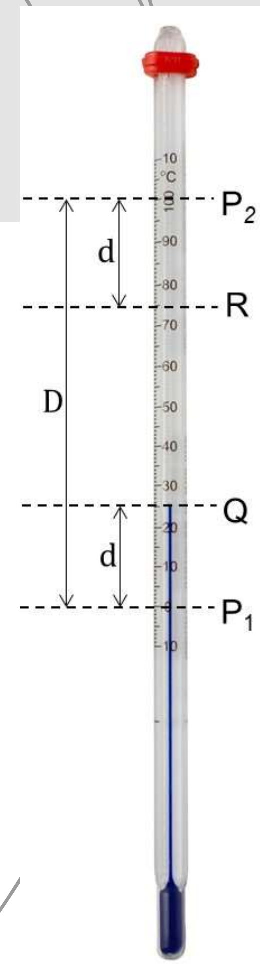
- Empirical temperature scales are ordinal scales:
  - Historic Fahrenheit mercury-based scale
  - Historic Celsius mercury-based scale
  - Callendar scale
  - ITS-27, ITS-48, IPTS-68 and ITS-90

Celsius mercury-based centigrade scale

- Celsius mercury-based centigrade scale (1741):
  - Put a mark P_1 corresponding to ice point
  - Put a mark P_2 corresponding to steam point
  - Divide the interval $\overline{P_1 P_2} = D$ into 100 equal intervals

- It is a perfectly defined ordinal scale:
  - It preserves equality and order
  - It does not preserve equal intervals (equal intervals do not correspond to equal differences in hotness)

- Assumes $t = 100 \cdot \frac{d}{D}$ (mercury does not expand linearly on temperature)



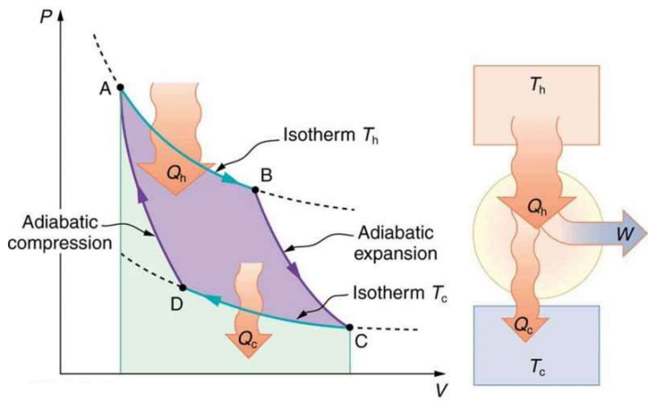
Carnot theorem (1824)

- Carnot theorem (1824): all Carnot engines (reversible cyclic heat engines) that operate between two thermostats at temperatures t_1 and t_2 have the same efficiency

$$\eta_R \equiv \frac{W}{Q_1} = 1 + \frac{Q_2}{Q_1}$$

$$\rightarrow \frac{Q_1}{Q_2} = f(t_1, t_2)$$

$$\rightarrow \frac{Q_1}{Q_2} = \frac{F(t_1)}{F(t_2)}$$

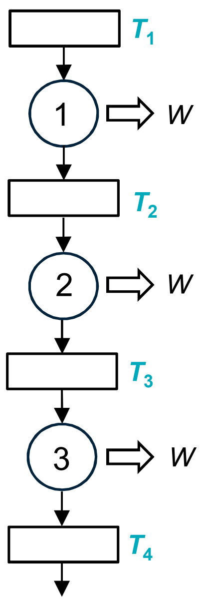


Nicolas Léonard Sadi Carnot (1796 - 1832)

- The ratio of the heats exchanged by the two thermostats is equal to the ratio of the same universal function of t, at t_1 and t_2

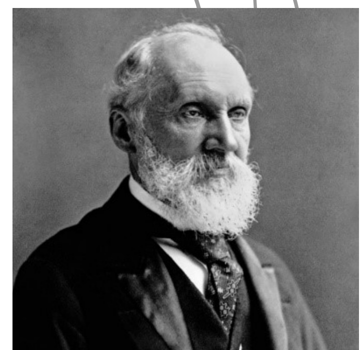
Thomson's proposal (1848)

- A cascade of Carnot engines, each producing the same mechanical work *W,* would operate between thermostats separated by the same temperature interval ΔT:



$$T_1 - T_2 = T_2 - T_3 = T_3 - T_4 = \cdots = \Delta T$$

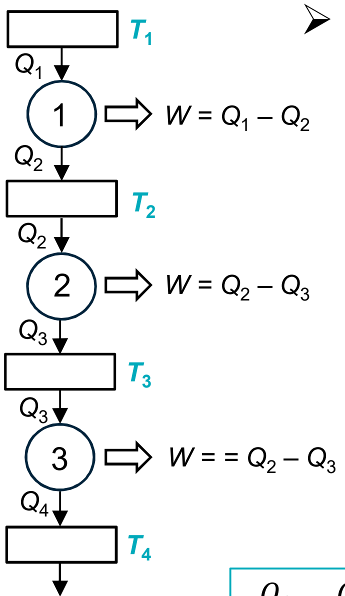
- **Each degree of temperature produces the same amount of mechanical work at any *T*** → Preserves equal intervals of hotness
- Absolute (independent from the physical properties of the working fluid)



Measurement theory:

- Thomson 1st proposal belongs to a 3rd type of measurement scale:
- **Interval scale** can establish:
  - Equality
  - Order
  - Equal intervals
  - Arbitrary zero

Thomson's proposal (1854)

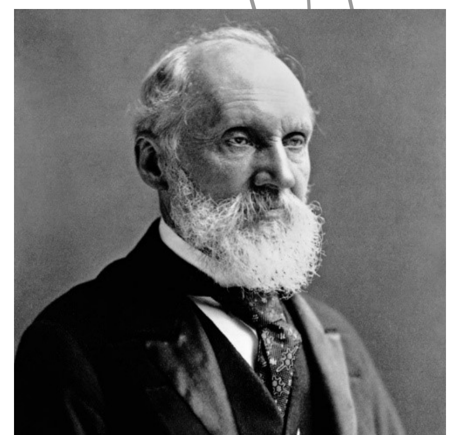


$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_3}{T_3}$$

- Thomson's proposal (1854):
  - make the simplest possible choice for F in $\frac{Q_1}{Q_2} = \frac{F(t_1)}{F(t_2)}$
  - $F(t) \equiv t \qquad t \rightarrow T \qquad \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$

Measurement theory:

- Thermodynamic temperature scale is a 4th type of measurement scale
- **Rational scale:**
  - Equality
  - Order
  - Equal Intervals
  - Equal ratios
  - Natural zero



Sir William Thomson,
1st Baron Kelvin of Largs
(1824 - 1907)

Evolutionary path of temperature scales

Nominal scale: Distinguished only between cold and warm

Snow is cold,
fire is hot

Ordinal scale: Different degrees of warmer and colder introduced

- hot
- warm
- cool
- chilly
- cold
- freezing

1724: Fahrenheit scale
1741: Celsius scale

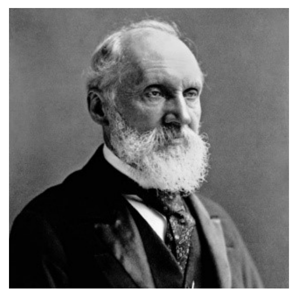
Interval scale:
Development of thermodynamics

1848: Thomson scale
Modern Fahrenheit scale
Modern Celsius scale

Rational scale:
Development of thermodynamics

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

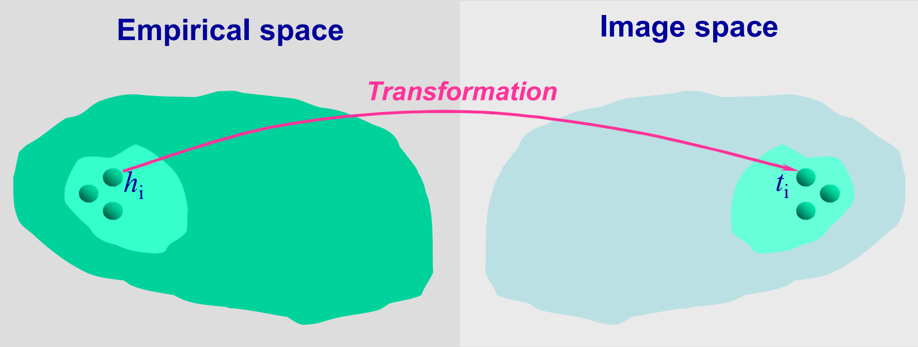
1854: Kelvin thermodynamic scale T_{TP} = 273.16 K



Evolution: the more we learnt about temperature and its true nature, the more the scale was able to encode the structure of temperature in the numbers we used to measure it

Measurement theory (representational)

- A measurement scale is a correspondence between:
  - the space of the quantity/magnitude/entity (hotness h_i)
  - the space of the numbers attributed to the quantity (t_i)



- **Measurement scale: assigns numbers to a quantity**
  - Relations exhibited by numbers (equality, difference, ratio, …) do not always correspond to meaningful relations among the quantities measured by those numbers
  - Numbers are adequate for expressing quantities only when the correspondence is one-to-one (homomorphism)

Types of measurement scale (Stevens, 1946)

Scale	Mathematical operations among numbers	Allowed scale transformations *f*: $x \rightarrow f(x)$	Examples
Nominal	equality	*f* any 1:1 function	Uniform numbers in a football team
Ordinal	equality order	f any monotonic function	Celsius and Fahrenheit, Rockwell hardness
Interval	equality order equal intervals	$f: x \rightarrow ax + b$	Thomson scale (1848), latitude and longitude,
Rational	equality order equal intervals equal ratios	$f: x \rightarrow ax$	Kelvin thermodynamic scale, length, mass

Operations

Scale	Mathematical operations among numbers	Allowed scale transformations *f*: *x* → *f(x)*	Examples
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➢ Scale operations with modern Celsius scale (interval scale)

- If we have 18 °C in Paris and 9 °C in Moscow,
  does it make sense to say that temperature in Paris is twice that in Moscow?

- If we have 18 °C in Paris, 9 °C in Moscow, 32 °C in Bangkok and 23 °C in Los Angeles,
  does it make sense to say that $T_{\text{Paris}} - T_{\text{Moscow}} = T_{\text{Bangkok}} - T_{\text{LosAngeles}}$

Transformations

Scale	Mathematical operations among numbers	Allowed scale transformations *f*: *x* → *f(x)*	Examples
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Ordinal	equality order	f any monotonic function	Celsius and Fahrenheit, Rockwell hardness
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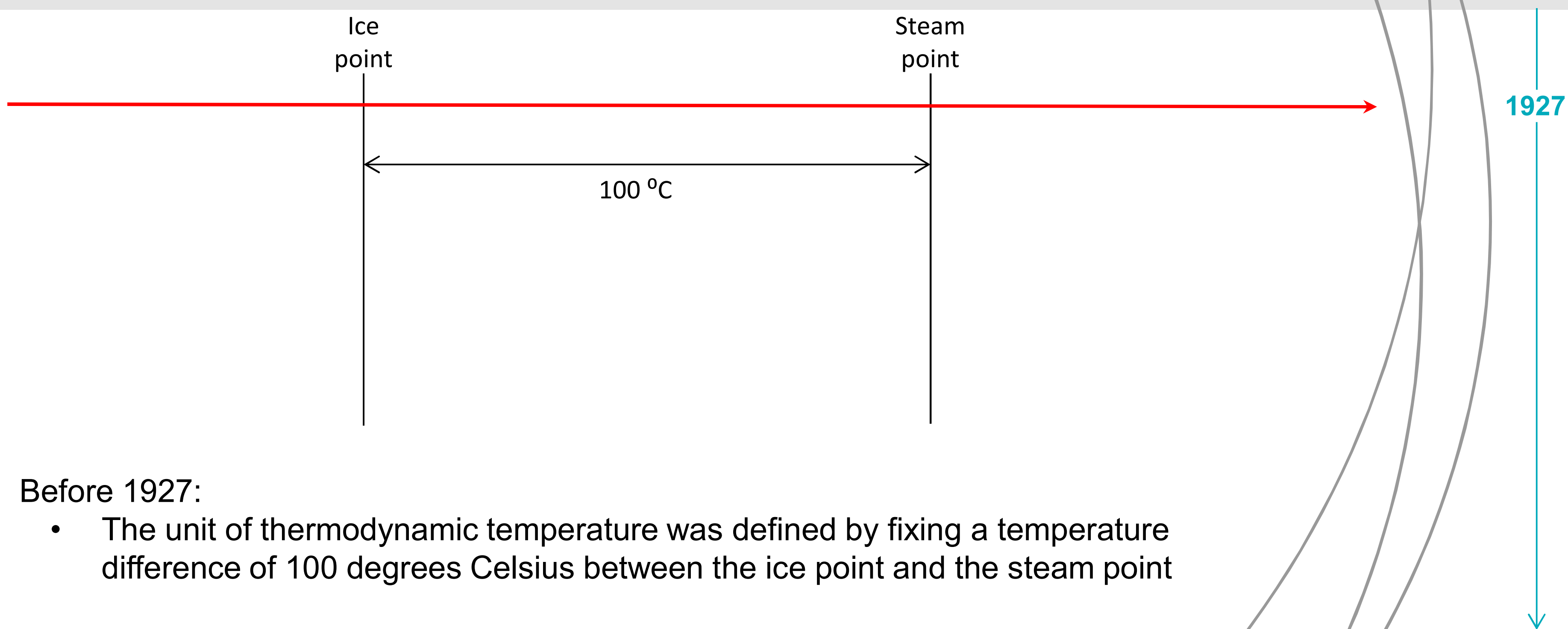
➢ Scale transformations

- Interval scale: from modern Celsius to Fahrenheit by applying *a* = 9/5 and *b* = 32
- Rational scale: in Kelvin thermodynamic scale change the triple point of water from 273.16 K to 7 K* by applying a = 7/273.16

Part 2

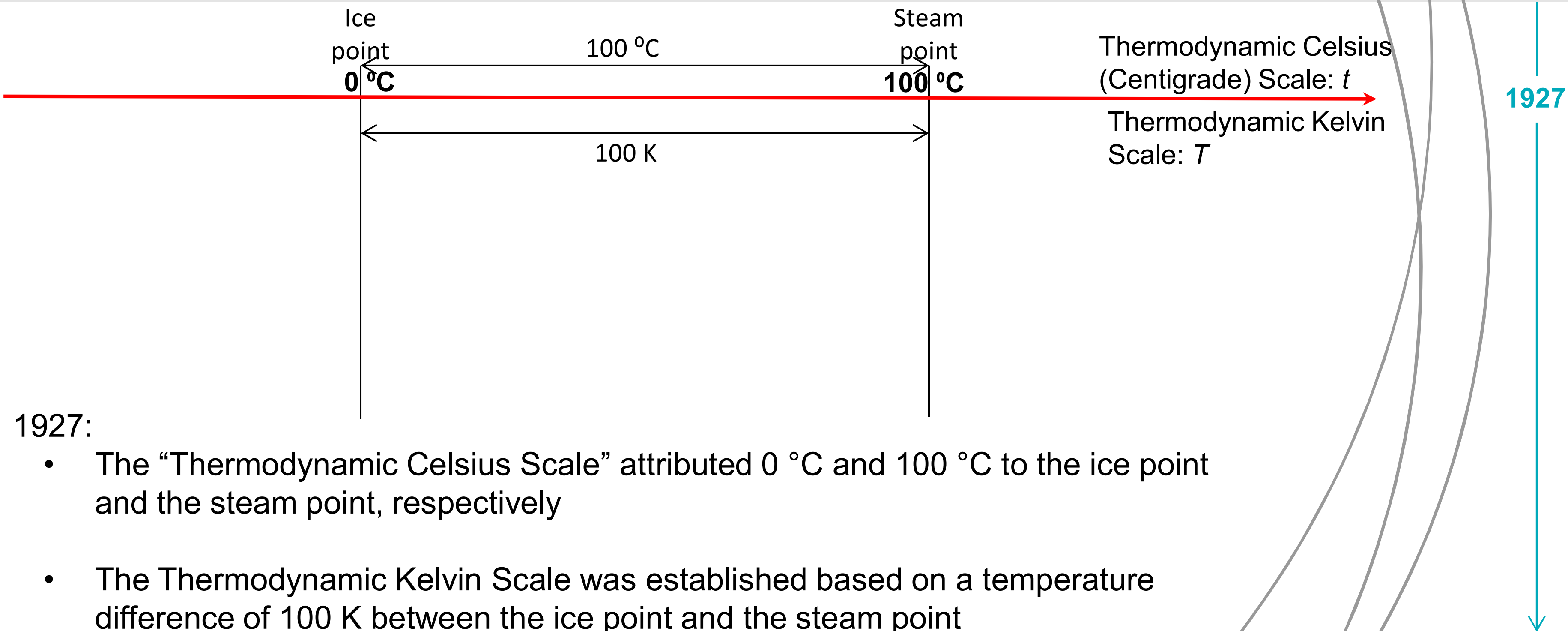
Evolution of the thermodynamic temperature scale

Evolution of the thermodynamic scale (1/12)



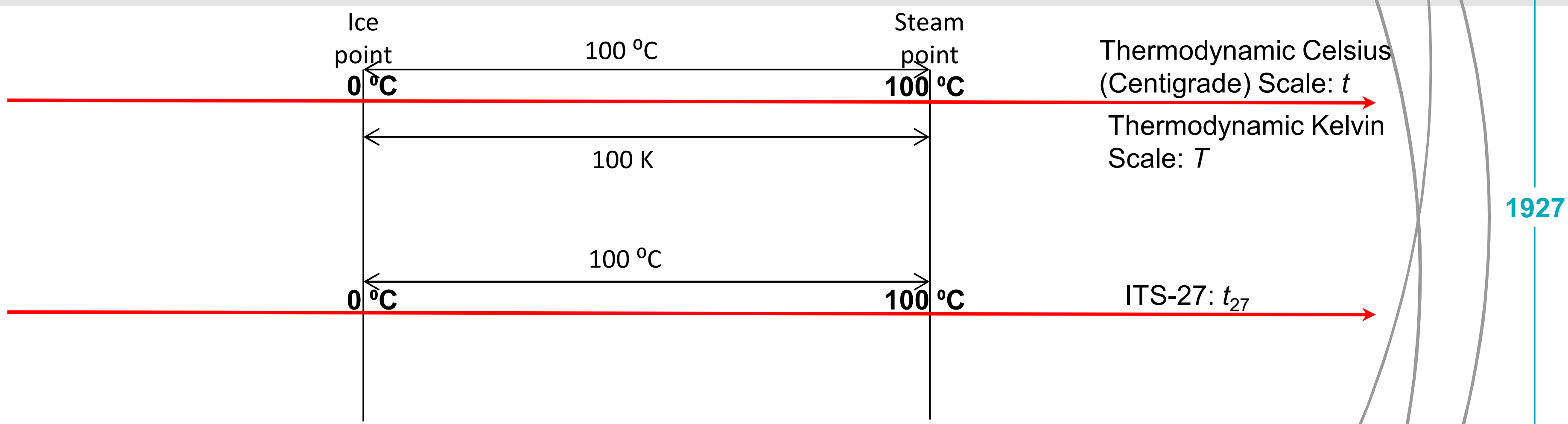
- Before 1927:
  - The unit of thermodynamic temperature was defined by fixing a temperature difference of 100 degrees Celsius between the ice point and the steam point

Evolution of the thermodynamic scale (2/12)



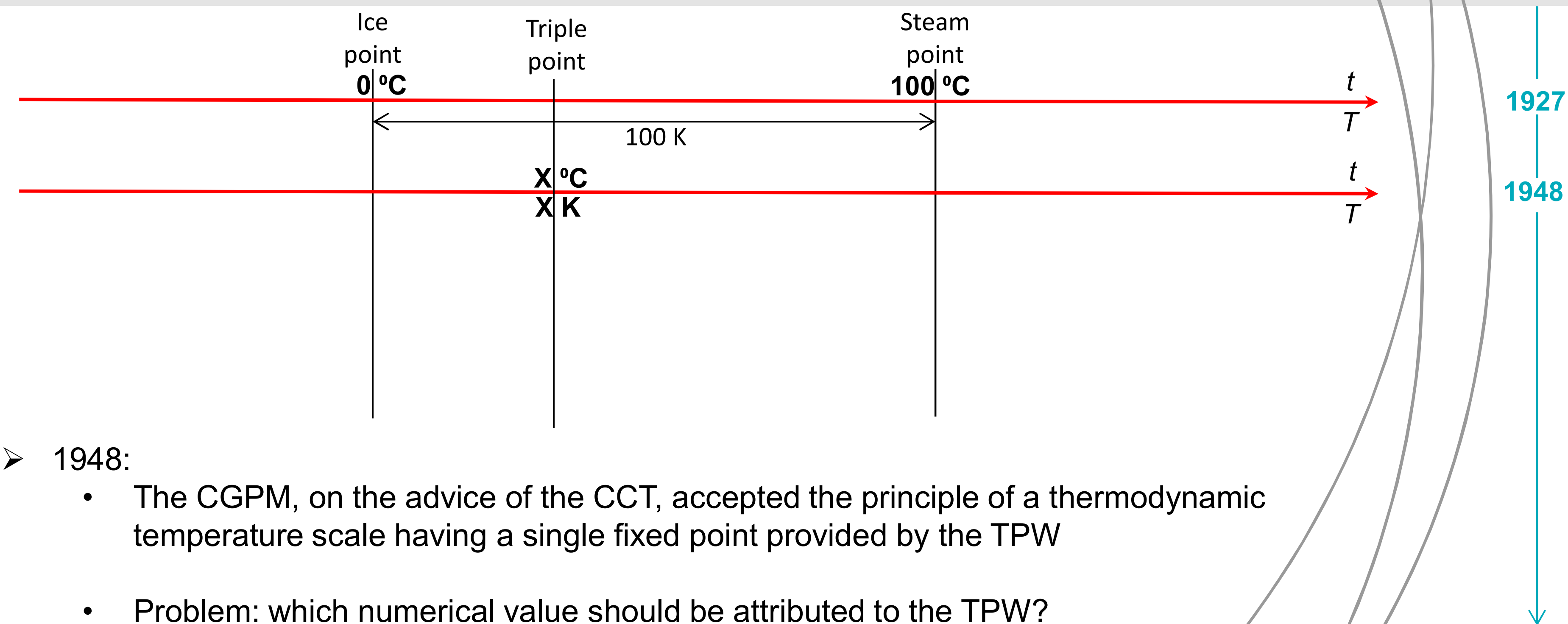
- 1927:
  - The "Thermodynamic Celsius Scale" attributed 0 °C and 100 °C to the ice point and the steam point, respectively
  - The Thermodynamic Kelvin Scale was established based on a temperature difference of 100 K between the ice point and the steam point

Evolution of the thermodynamic scale (3/12)



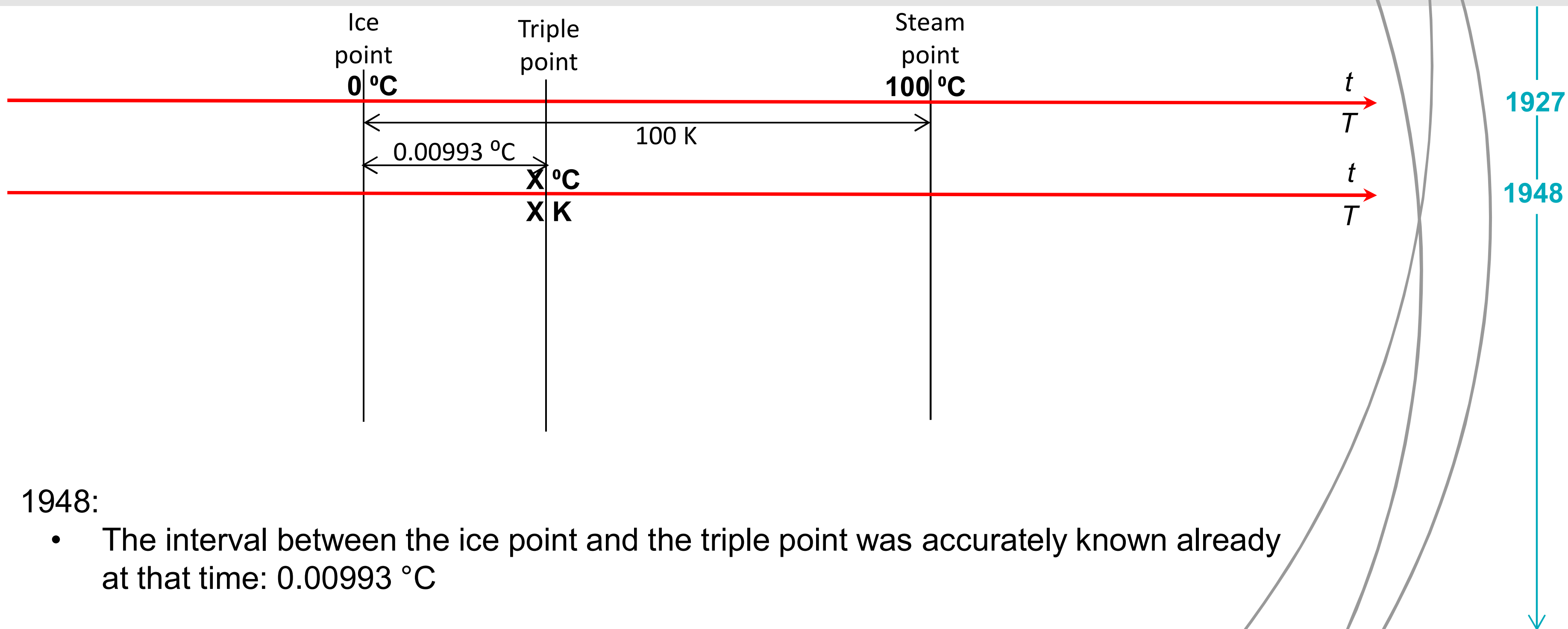
- 1927:
  - The International Temperature Scale of 1927 (ITS-27) attributed 0 °C and 100 °C to the ice point and the steam point, respectively.
  - The units of t, T and t_{27} were identical

Evolution of the thermodynamic scale (4/12)



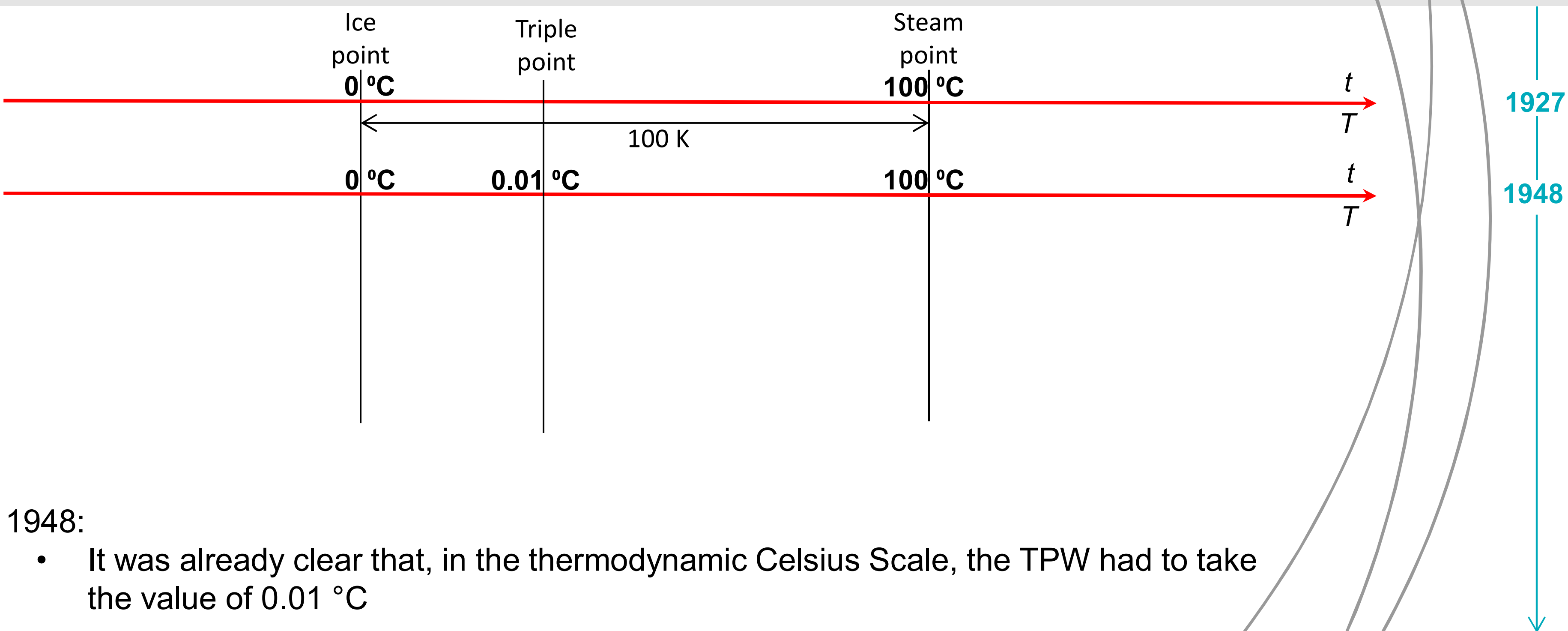
- 1948:
  - The CGPM, on the advice of the CCT, accepted the principle of a thermodynamic temperature scale having a single fixed point provided by the TPW
  - Problem: which numerical value should be attributed to the TPW?

Evolution of the thermodynamic scale (5/12)



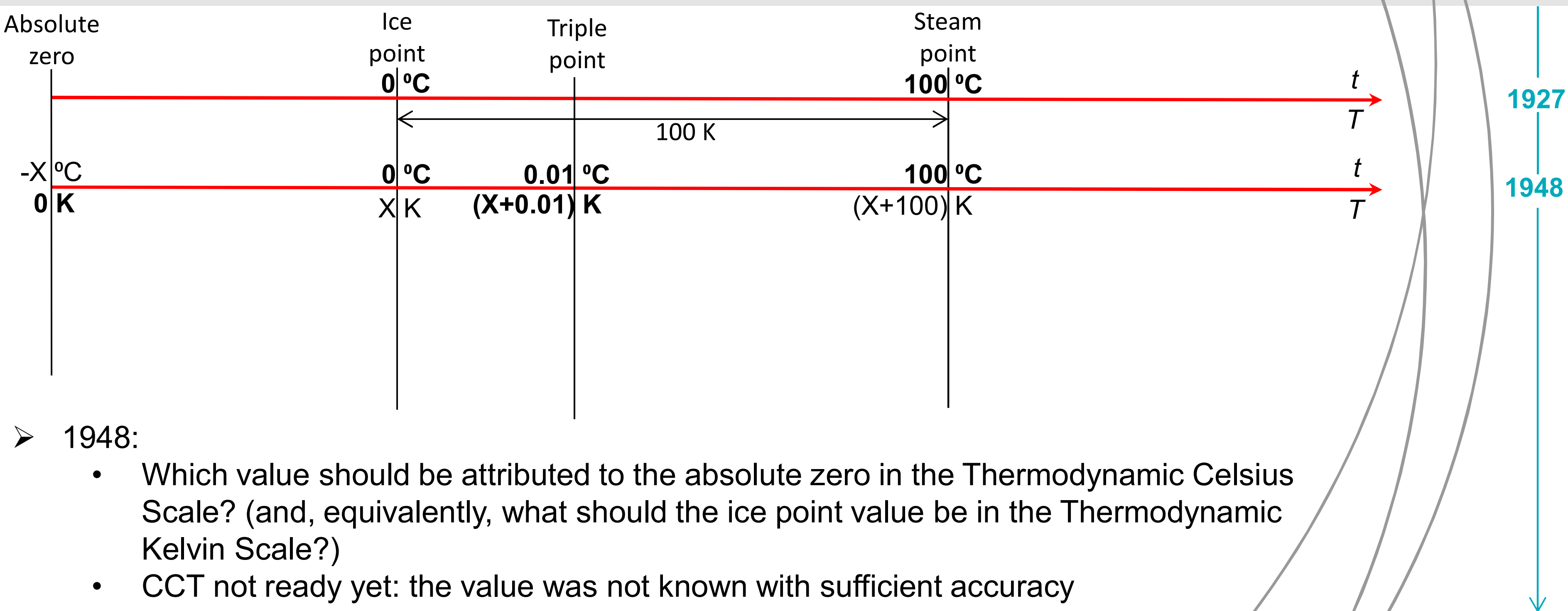
- 1948:
  - The interval between the ice point and the triple point was accurately known already at that time: 0.00993 °C

Evolution of the thermodynamic scale (6/12)



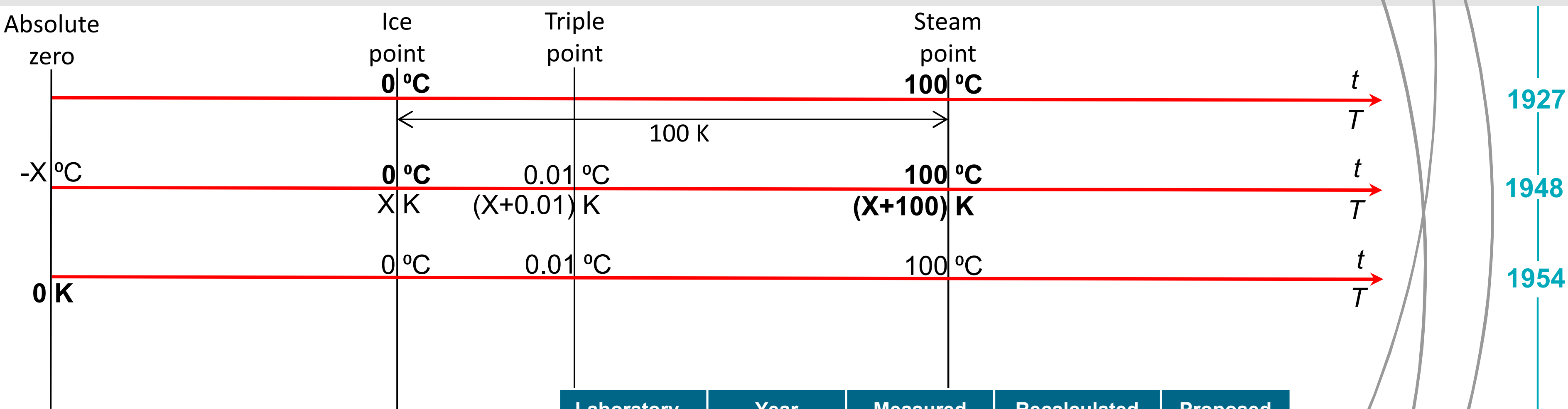
- 1948:
  - It was already clear that, in the thermodynamic Celsius Scale, the TPW had to take the value of 0.01 °C

Evolution of the thermodynamic scale (7/12)



- 1948:
  - Which value should be attributed to the absolute zero in the Thermodynamic Celsius Scale? (and, equivalently, what should the ice point value be in the Thermodynamic Kelvin Scale?)
  - CCT not ready yet: the value was not known with sufficient accuracy

Evolution of the thermodynamic scale (8/12)

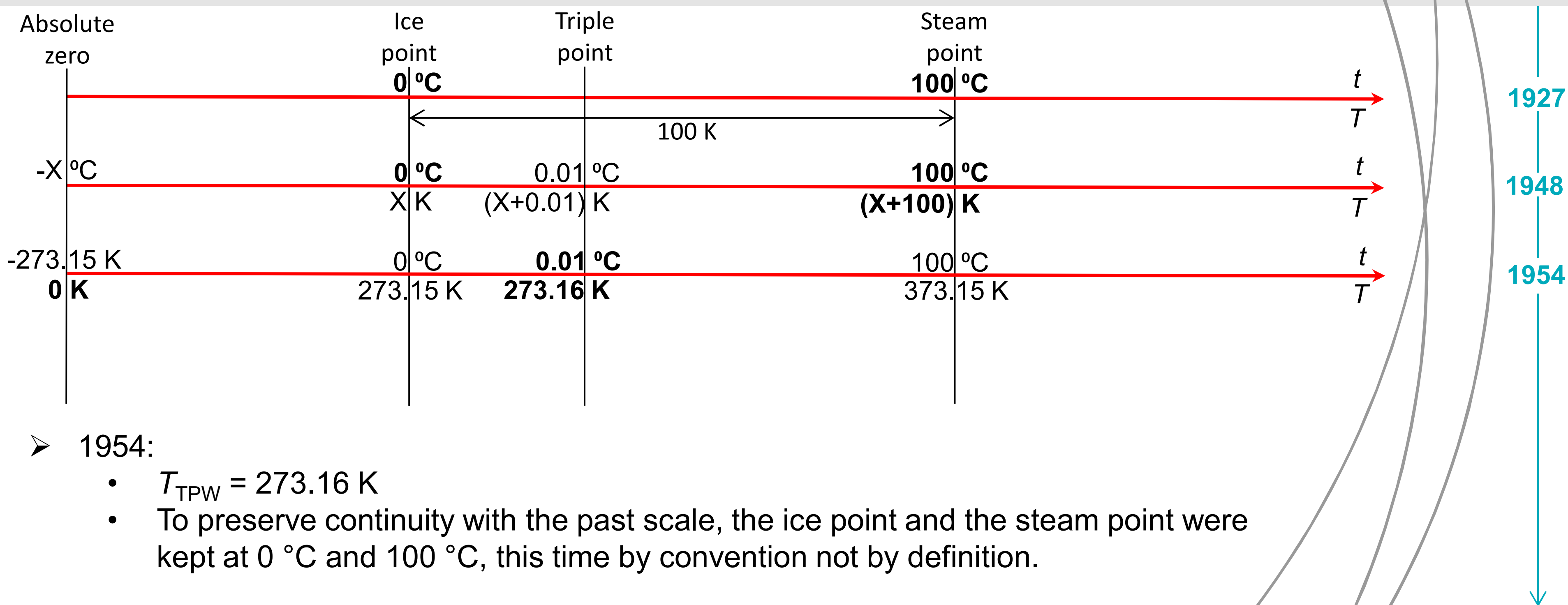


Laboratory	Year	Measured	Recalculated	Proposed
PTB	1929-1930	273.158	273.149	273.15
KOL	1934	273.147	273.149	273.15
TIT	1937-1942	273.144	273.148	273.15
MIT	1939-1952	273.174	273.174	273.17

$u(\theta_i) \approx 0.01$ °C

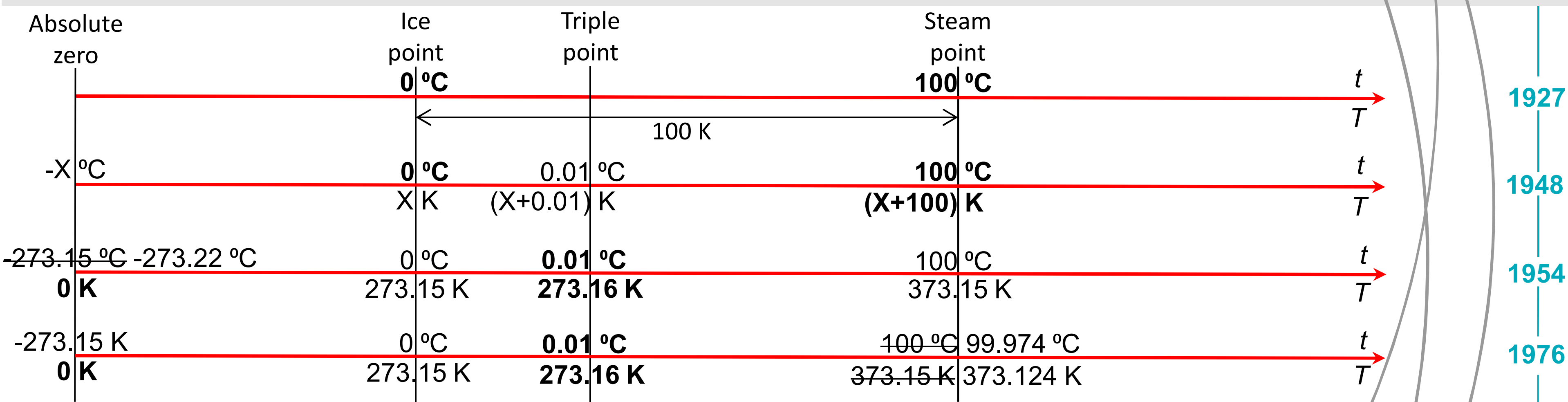
Thermodynamic temperature of the ice point
CCT, Session de 1954, Rapport et Annexes

Evolution of the thermodynamic scale (9/12)



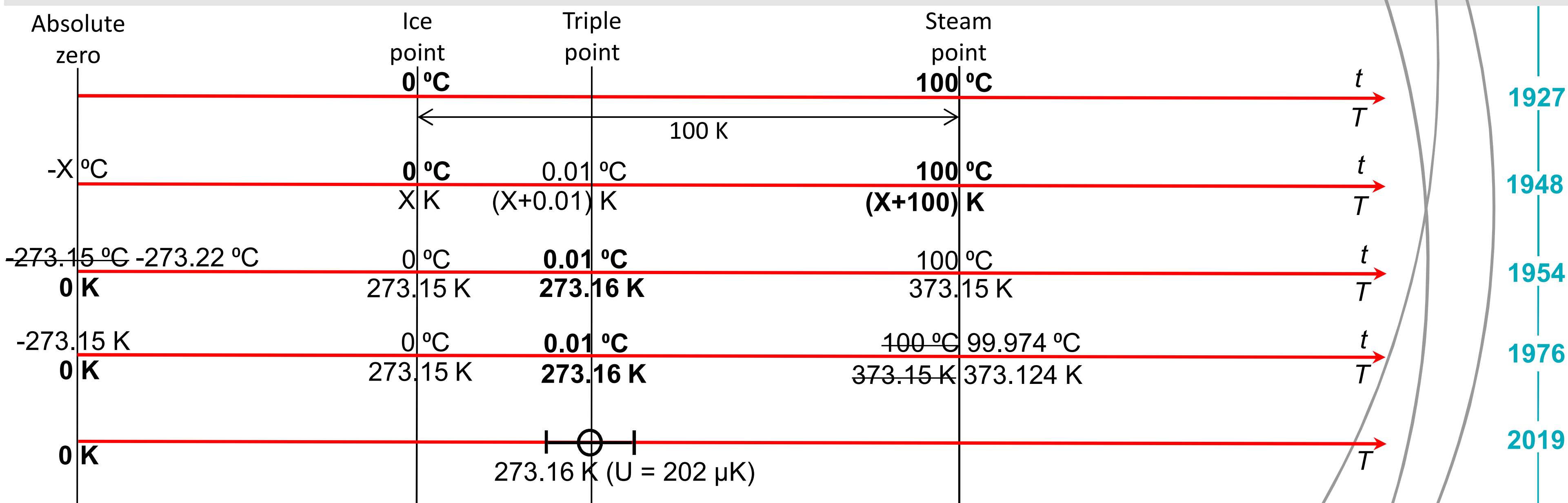
- 1954:
  - T_{TPW} = 273.16 K
  - To preserve continuity with the past scale, the ice point and the steam point were kept at 0 °C and 100 °C, this time by convention not by definition.

Evolution of the thermodynamic scale (10/12)



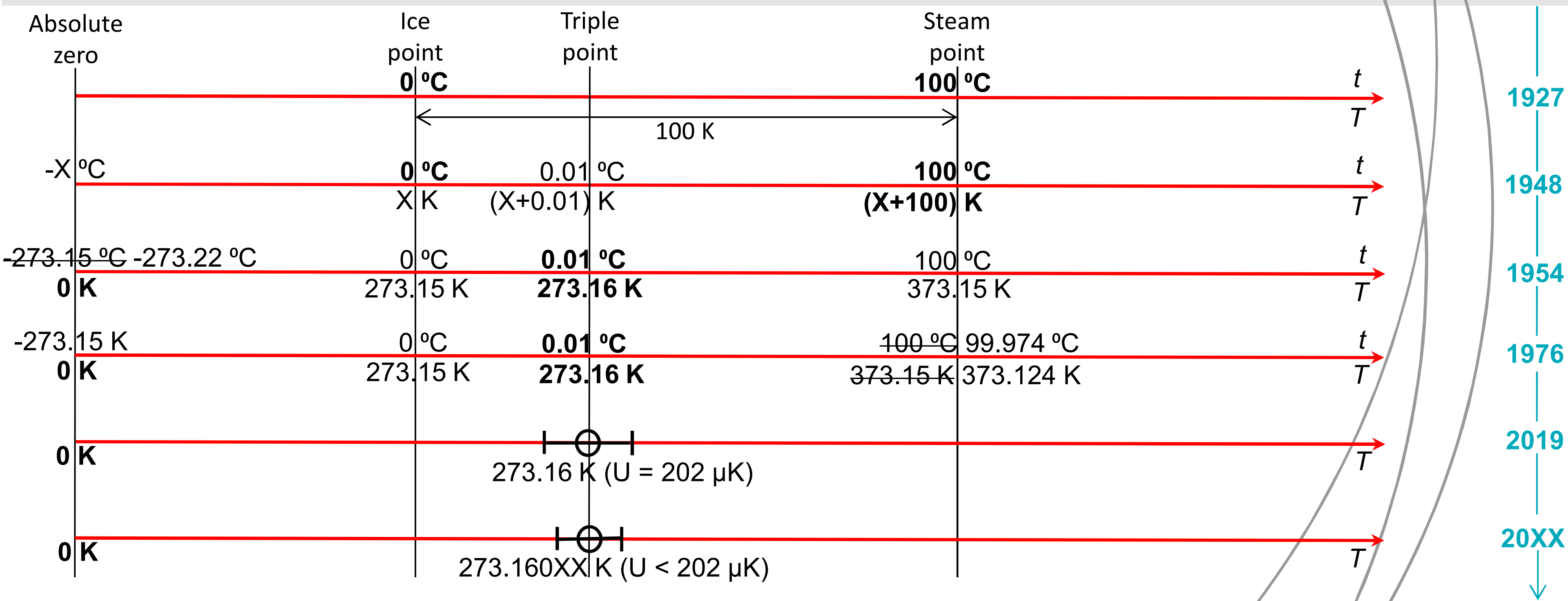
- 1976: t_S = 99.974 ºC (L.A. Guildner, R.E. Edsinger, *J. Res. Natl. Bur. Stand.* 1976, 80A, 703-738)
  - The size of the kelvin in the new thermodynamic scale is different (larger) from the size of the kelvin in the old thermodynamic scale
  - To maintain T_i = 0 ºC and T_S = 100 ºC in the thermodynamic Celsius scale, the absolute zero should have been -273.22 ºC

Evolution of the thermodynamic scale (11/12)



- 2019:
  - T_{TPW} = 273.16 K not by definition (standard relative uncertainty $3.7 \cdot 10^{-7}$)

Evolution of the thermodynamic scale (12/12)



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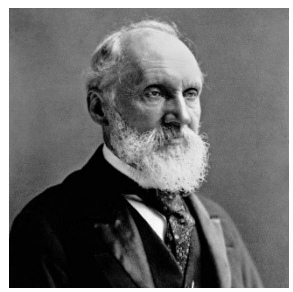

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Conclusions

- What has changed since 2019:
  - in the thermodynamic temperature scale
  - in the definition of thermodynamic temperature that the scale assumes
- Type of scale: unchanged, still a rational scale
  - TPW value can change, without affecting the size of the kelvin (because the size of the kelvin is not linked anymore to the TPW value)
- Size of the unit: change not perceptible
  - 2 μK at TPW and 9 μK at Ag fixed point
- Definition (meaning) of temperature: basically unchanged
  - Temperature is the average thermal energy per degree of freedom in the system
  - Not only a *thermodynamic* temperature but also a *statistical thermodynamic* temperature

Acknowledgement

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- Richard Rusby (correspondence)

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THANK YOU

Andrea Peruzzi: andrea.peruzzi@nrc-cnrc.gc.ca

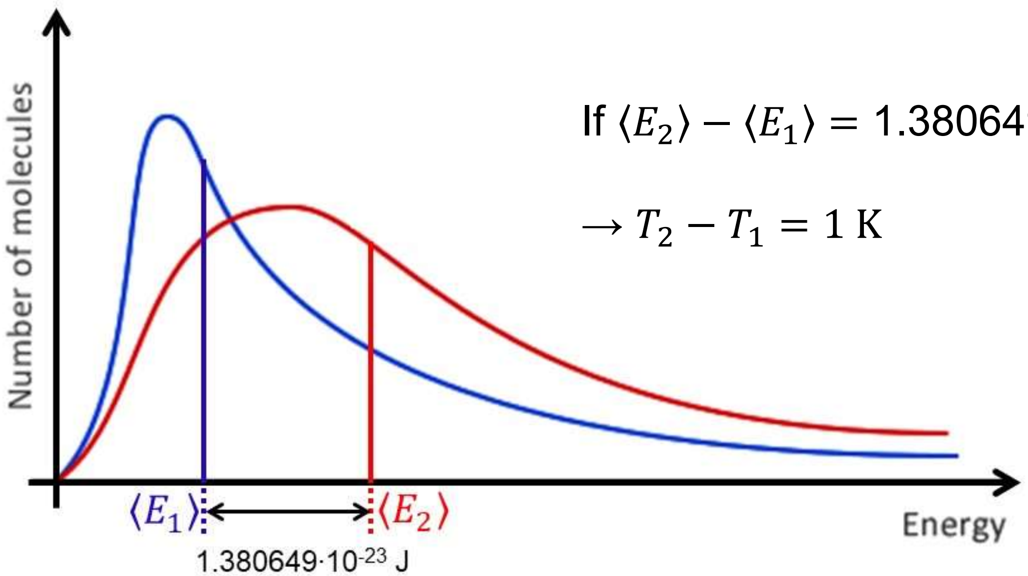
Consistency between the old and the new unit

- Old kelvin (before 20 May 2019):
  - TPW is the exactly known defining constant $T_{TPW} = 273.16 \cdot K_{old}$
- New kelvin (after 20 May 2019):
  - TPW is inexactly known $T_{TPW} = \text{X} \cdot K_{new}$
- T_{TPW} does not depend on the SI unit adopted: $273.16 \cdot K_{old} = \text{X} \cdot K_{new}$
- Consistency factor *f*: $\text{f} = \frac{X}{273.16} = \frac{T_{TPW}/X}{273.16} = \frac{k_{old}}{k_{new}}$

	k_{old}	k_{new}	*f*	µK at TPW	µK at Ag
CODATA 2017	$1.38064901 \times 10^{-23}$	1.380649×10^{-23}	1.000000007	2	9
CODATA 2014	$1.38064852 \times 10^{-23}$	1.380649×10^{-23}	0.999999652	95	

Definition of the kelvin

The kelvin is:
the change of thermodynamic temperature that results in a change of mean thermal energy of $1.380649 \cdot 10^{-23}$ J for the molecules of the system



If $\langle E_2 \rangle - \langle E_1 \rangle = 1.380649 \cdot 10^{-23}$ J

$\rightarrow T_2 - T_1 = 1\ \mathrm{K}$