

01. Inventing Temperature: Chap 1.

1. Fixed Points.

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2. Superheating
3. Theories of Boiling
4. Validation of Standards
6. Ontological Status of Fixed Points

- 1693. State of the art in thermometers:



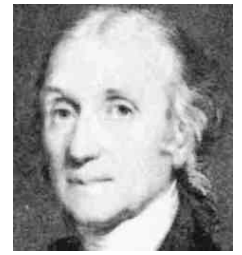
Edmond Halley
(1656-1742)

"I cannot learn that any of them...were ever made or adjusted, so as it might be concluded, what the Degrees or Divisions...did mean; neither were they ever otherwise graduated, but by Standards kept by each particular Workman, without any agreement or reference to one another."

- Fixed point = phenomenon known to take place always at the same temperature and that thus can be used as a thermometric benchmark.
- Problem: "...to ensure the stability and usefulness of thermometers, we must be quite certain that the presumed fixed points are actually fixed sharply..." (Chang, pg. 9).

Person	Year	Fixed points
Sanctorius	c.1600	candle flame <i>and</i> snow
Accademia del Cimento	c.1640?	most severe winter cold <i>and</i> greatest summer heat
Otto Von Guericke	c.1660?	first night frost
Robert Hooke	1663	freezing distilled water
Robert Boyle	1665?	congealing oil of aniseed <i>or</i> freezing distilled water
Christiaan Huygens	1665	boiling water <i>or</i> freezing water
Honoré Fabri	1669	snow <i>and</i> highest summer heat
Francesco Eschinardi	1680	melting ice <i>and</i> boiling water
Joachim Dalencé	1688	freezing water <i>and</i> melting butter <i>or</i> ice <i>and</i> deep cellars
Edmond Halley	1693	deep caves <i>and</i> boiling spirit
Carlo Renaldini	1694	melting ice <i>and</i> boiling water
Issac Newton	1701	melting snow <i>and</i> blood heat
Guillaume Amontons	1702	boiling water
Ole Rømer	1702	ice/salt mixture <i>and</i> boiling water
Phillippe de la Hire	1708	freezing water <i>and</i> Paris Observatory cellars
Daniel Fahrenheit	c.1720	ice/water/salt mixture & ice/water mixture & healthy body temp
John Fowler	c.1727	freezing water <i>and</i> water hottest to be endured by a hand held still
R.A.F. de Réaumur	c.1730	freezing water
Joseph-Nicolas D l'Isle	1733	boiling water
Anders Celsius	by 1741	melting ice <i>and</i> boiling water
J. B. Micheli du Crest	1741	Paris Observatory cellars <i>and</i> boiling water
<i>Encyc. Britannica</i>	1771	freezing water <i>and</i> congealing wax

- 1776. Royal Society of London forms committee to make recommendations for fixed points for thermometers.



Henry Cavendish
(1731-1810)

Two problems with fixity of boiling point of water:

- Varies widely with atmospheric pressure.
 - *Recommendation: Adopt standard pressure of 29.8 inches of mercury.*
- Mercury in stem of thermometer is not necessarily at same temp as mercury in bulb.
 - *Recommendation: Submerge thermometer completely, either in boiling water or in steam from boiling water.*
- Bigger Problem: There are different temperatures associated with different degrees of boiling!



Jean-André De Luc
(1727-1817)

"When water begins to boil, it does not yet have the highest degree of heat it can attain. For that, the entire mass of the water needs to be in movement; that is to say, that the boiling should start at the bottom of the vessel, and spread all over the surface of the water, with the greatest impetuosity possible. From the commencement of ebullition to its most intense phase, the water experiences an increase in heat of more than a degree."

- 1772. De Luc's *Inquiries on the Modifications of the Atmosphere*.
- "True ebullition" = phenomenon in which the 'first layer' of water in contact with heat source became saturated with the maximum possible amount of heat...thereby turning into vapor and rising up through the water as bubbles.

(a) Introduce drops of water into hot oil and determine the temperature of the oil at which the drops explode into vapor.

○ Result: 112°C.

(b) Place water in glass flask and heat slowly in an oil bath.

○ Result: Large bubbles at 100°C and over 103°C; steady boil at 101.9°C.

- Problem: Dissolved air induces ebullition-like phenomenon before true-ebullition occurs.

(c) Remove dissolved air through boiling and shaking.

○ Result: Steady boil in oil bath at 140°C!

- But: Inserting thermometer re-introduces air into water.
- So: Need to purge water with thermometer already inserted...

"The operation lasted 4 weeks, during which I hardly ever put down my flask eept to sleep, to do business in town, and to do things that required both hands. I ate, I read, I wrote, I saw my friends, I took my walks, all the while shaking my water..."



- Result: In a vacuum, pure water boils at 97.5°C; at normal atmospheric pressure, pure water boils at 112.°2C!

Candidates for "boiling"

1. *Common boiling*. Bubbles rise at steady rate, varying degrees of vigor.
2. *Hissing*. Bubbles rise partway and condense before reaching surface (tea kettle singing).
3. *Bumping*. Large isolated occasional bubbles; unstable temperatures.
4. *Explosion*. Large portion of water erupts into vapor. (Extreme case of bumping.)
5. *Fast evaporation only*. No bubbles.
6. *Bubbling*. Escape of dissolved air (as in carbonated drinks).

2. Superheating.

- 1812. Joseph-Louis Gay-Lussac: Water boils at 101.232°C in a glass vessel, and at 100.000°C in a metallic vessel.
 - *Throwing in finely powdered glass into glass vessel brings boiling temp down to 100.329°C .*
 - *Throwing in iron filings brings it down to 100.000°C .*
- 1842. François Marcet: Superheating in ordinary water beyond 105°C with glass vessels previously containing sulphuric acid.
- 1846. François Marie Louis Donny: Superheating at 137°C .
- 1861. Louis Dufour: Superheating of drops of water in other liquids at 178°C .
- 1869. Georg Krebs: Superheating at 200°C .



Joseph-Louis Gay-Lussac
(1778-1850)

"All investigators now agreed that the raising of temperature to the 'normal' boiling point was not a sufficient condition to produce boiling. What they could not agree on was what the additional conditions needed for the production of boiling were." (Chang, pg. 22.)

Why was the boiling point of water still feasible as a fixed point?

(1) The temperature of superheated water falls as soon as boiling commences.

- So: *The high temps associated with superheating are irrelevant.*

(2) The prevention of superheating was easy.

"If one left naturally occurring water in its usual state full of dissolved air...and if one left the container vessels just slightly dirty or rough...and if one did not do anything else strange like isolating the water from solid surfaces, then common boiling did take place" (Chang, pg. 23).

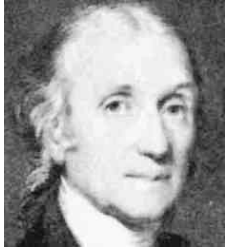
(3) The temperature of steam was a good indicator of the common boiling point.



Henry Cavendish

"The most accurate way of adjusting the boiling point is, not to dip the thermometer into the water, but to expose it only to the steam, in a vessel closed up in the manner represented."

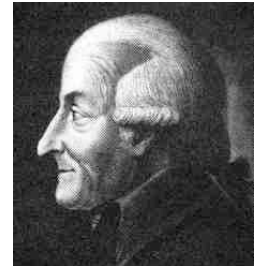
- 1777. Cavendish in an unpublished paper:



"Water as soon as it is heated ever so little above that degree of heat which is acquired by the steam of water boiling in vessels closed as in the experiments tried at the Royal Society, is immediately turned into steam, provided that it is in contact either with steam or air; this degree I shall call the boiling heat, or boiling point...if the water is not in contact with steam or air, it will bear a much greater heat without being changed into steam, namely that which Mr. De Luc calls the heat of ebullition."

- 1777. De Luc disagrees in correspondence:

"Setting aside for a moment all theory, it seems that the heat of the vapor of boiling water can be considered only with difficulty as more fixed than that of the water itself; for they are so mixed in the mass before the vapor emerges that they appear to have no alternative but to influence the temperature of each other..."



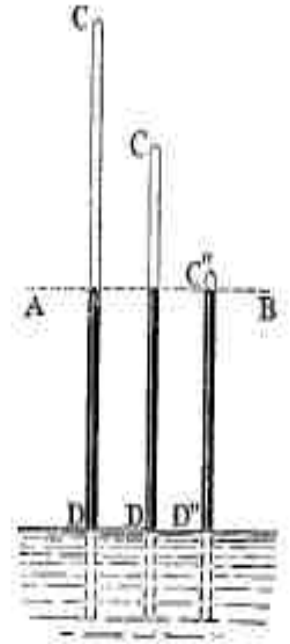
- But: Marcet (1842) confirms fixity of the "steam point": For water boiling at over 105°C, steam temperature was only a few tenths of a degree over 100°C.

What Explains This?

3. Theories of Boiling.

- c.1757. Cavendish observes a dependence between the pressure of water vapor and its temperature:

- *At constant temperature, the larger the volume, the greater the vapor pressure (and vice versa).*
- *If the temperature is increased, and the volume is held constant, the vapor pressure increases (and vice versa).*



- Moreover: The vapor pressure of water is equal to the normal atmospheric pressure at 100°C.
 - *Confirmed later by Dalton 1802, Biot 1816, Regnault 1847.*

The "Pressure-Balance Theory of Boiling":

- Boiling takes place when the water produces vapor with sufficient pressure to overcome the resistance of the external atmosphere.

Modified by the Adhesion Hypothesis:

- 1818. Gay-Lussac.

- *Boiling is retarded by the adhesion of water to the vessel and also by the cohesion of water with itself.*

- 1842. Marcet:

- *Achieves boiling at 99.85°C in a glass vessel with drops of sulphur.*
- *When bottom and sides are covered with a thin layer of gomme laque (shellac), boiling takes place at 99.67°C.*

- 1861. Dufour dissents:

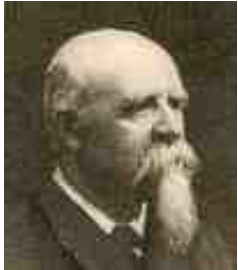
- *Observes extreme superheating of water drops removed from solid surfaces by suspension in other liquids.*

- Marchel Emile Verdet (1824-1866):

- *Suggests boiling is provoked not by all solid surfaces but only by "unwetttable" surfaces that possess microscopic roughness.*

- 1866 & 1875. Désiré Gernez: Presence of internal gases is crucial enabling condition for boiling.

- *Boiling can be induced in superheated water by the insertion of trapped pockets of air.*



"The explanation of the phenomenon of boiling that De Luc proposed was so clear and conformable to reality, that it is astonishing that it was not universally adopted."



- 1868-69. Charles Tomlinson: Crucial enabler is not gases but small solid particles.

- *Metallic cage lowered in water does not induce boiling if it's clean, even though it contains pockets of air.*

- "It really does seem to me that too much importance has been attached to the presence of air and gases in water and other liquids as a necessary condition of their boiling."

- "A liquid at or near the boiling point is a supersaturated solution of its own vapor, constituted exactly like soda-water, Seltzer-water, champagne, and solutions of some soluble gases."

- 1880-81. John Aitken's "On Dust, Fogs, and Clouds".

- *In absence of dust, steam can be cooled below the temperature indicated by the standard pressure-temperature relation without condensing into water.*



John Aitken

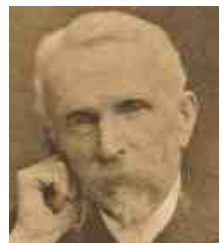
"If there was no dust in the air there would be no fogs, no clouds, no mists, and probably no rain..."

- Thus: Steam point is no more fixed than boiling point of liquid water.

"Now we can see that it was only some peculiar accidents of human life that gave the steam point its apparent fixity: air on earth is almost always dusty enough, and no one had thought to filter the air in the boiling-point apparatus" (Chang, pg. 36).

- Aitken: "boiling point" = "the temperature at which evaporation takes place into an atmosphere of its own vapour at the standard atmospheric pressure of 29.905 inches of mercury."

"Where, then, it may be asked, is the difference between boiling and evaporation? None, according to this view. Boiling is evaporation in presence of only its own vapour; and what is usually called evaporation is boiling in presence of a gas."



4. Validation of Standards.

- Thermometers require fixed points: How can fixed points be established?

What is a measurement scale?

- An assignment of numbers to things according to a determinative, non-degenerative rule. (Ellis 1968; Skow 2011)

Caution: Typically, numbers have properties: Order relations, arithmetic operations, etc. When we assign numbers to things, the things may not have as many properties as the numbers.



Scale	Number property	Invariant under:	Provides answer to:
<i>Nominal</i>	Labels.	Permutations.	
<i>Ordinal</i>	Labels and ordering.	Arbitrary monotonic increasing function.	<i>Is the temp at which water boils greater than the temp at which it freezes?</i>
<i>Interval</i>	Labels, ordering, interval ratios. $f(x, y, z, w) = x - y / z - w $	$x' = ax + b$	<i>Is the temp difference between the sun and the earth greater than the temp difference between a cup of tea and the surrounding air?</i>
<i>Ratio</i>	Labels, ordering, interval ratios, number ratios. $g(x, y) = x/y$	$x' = ax$	<i>Is there a natural zero point for temperature?</i>

- *Thermometer* = furnishes a *numerical* temperature scale (interval or ratio).
- *Thermoscope* = a device capable of measuring a difference in temperature.
 - *Furnishes an ordinal temperature scale; provides standard for identifying fixed points.*



- Thermoscopes assume the reliability of human sensation: How can human sensation be justified?

Ex: Put one hand in hot water and other in cold water. Then put both in uniformly lukewarm water. One hand feels the water is cool, the other feels it is warm. A thermoscope corrects our judgement by telling us that the lukewarm water has uniform temperature.

"Principle of Respect": "...[O]ur use of instruments is made with a respect for sensation as a prior standard, but that does not mean that the verdict of sensation has unconditional authority." (Chang, pg. 43).

Relation between prior and later standards: "The later standard is neither deduced from the prior one, nor derived from it by simple induction or generalization. It is not even a relation of strict consistency, since the later standard can contradict the earlier one. The constraint on the later standard is that it should show sufficient agreement with the prior standard... 'sufficient' should be understood as an indication of intent, to respect the prior standard as far as it is plausible to do so." (Chang, pg. 44.)

- How can a later standard (*e.g.*, thermoscope) correct a prior standard (*e.g.*, human sensation) which serves as a justification for the later standard?

Chang's Notion of "Epistemic Iteration":

"...a process in which successive stages of knowledge, each building on the preceding one, are created in order to enhance the achievement of certain epistemic goals." (Chang, pg. 45.)

The Iterative Development of Temperature Standards:

- *Stage 1.* Bodily sensation of hot and cold.
- *Stage 2.* Thermoscopes using the expansion of fluids.
- *Stage 3a.* Numerical thermometers based on freezing and boiling water as fixed points.
- *Stage 3b.* Numerical thermometers with boiling point replaced by steam point.

5. Ontological Status of Fixed Points.

- Don't occur "naturally": Boiling temperature of water is not fixed!
- Are they artificially created simply to serve theoretical purposes?
 - *How do we create the circumstances underwhich we are justified in saying "Water boils at 100°C"?*

Epistemic strategies in defense of fixity:

- (1) If causes of variation can be eliminated, do so.
- (2) If causes of variation cannot be eliminated but can be indentified and quantified, learn to make corrections.
- (3) Ignore small, inexplicable variations, and hope they go away.

Serendipitous Robustness:

"The most important serendipitous factor for the fixity of the boiling point is the fact that water on earth normally contains a good deal of dissolved air. For the steam point, it is the fact that air on earth normally contains a good deal of suspended dust." (Chang, pg. 50.)

- *Such serendipitous factors are independent of theory.*
- Claim: Sense-data and high-level theories are not robust over time:
 - *Interpretation of sense-data is conditioned by theoretical frameworks (theory-ladenness of observations).*
 - *Theories change over time.*

On the other hand: "No matter how drastically high-level theories change, some *middle-level regularities* [like fixed points] may remain relatively unaffected, even when their deep theoretical meanings and interpretations change significantly." (Chang, pg. 52.)