04. Inventing Temperature: Chap 4.

1. Theories of Heat Prior to TD
2. Thomson's 1st Concept of Abs. Temp.
3. Thomson's 2nd Concept of Abs. Temp.
4. Operationalizing Abs. Temp.
5. Operationalism
6. Accuracy Through Iteration

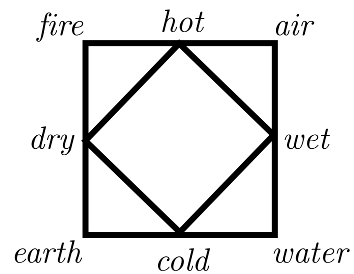
1. Theories of Heat Prior to Thermodynamics.

Aristotle (384-322 B.C.)

- Cold and Hot as contrary qualities (forms).
- *Contrary forms* = forms that cannot both be present in the same thing.
- Forms change *via* transitions between contraries.

Element	*Form*
earth	cold/dry
water	cold/wet
air	hot/wet
fire	hot/dry

cold ⇔ hot	*wet ⇔ dry*
water ⇔ air	water ⇔ earth
earth ⇔ fire	air ⇔ fire



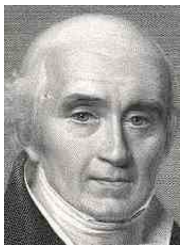
The Mechanical Philosophy

- Gassendi: Mechanical philosophy, atomist version.
- Calorific atoms cause heat by agitating matter particles.
- Frigorific atoms clog pores of bodies and obstruct motion of matter particles.

Pierre Gassendi
(1592-1655.)

1791. Pictet's Experiment

- Two concave mirrors facing each other; thermometer at focus of one, hot object at focus of other.
  - *Thermometer rises immediately.*
- ***Conclusion***: Radiation of heat at extremely high speed.
- Replace hot object with flask of snow.
  - *Thermometer drops immediately*
  - *Radiation of cold at extremely high speed?*

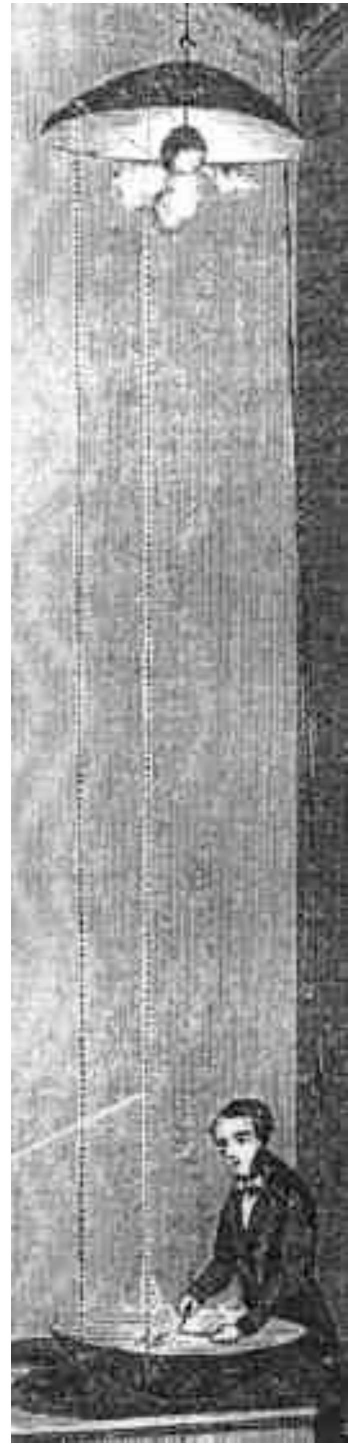


Marc-Auguste Pictet
(1752-1825)

Heat radiates away from thermometer towards ice.

"Any considerable increase of heat gives us the idea of positive warmth or hotness, and its diminution excites the idea of positive cold. Both these ideas are simple, and each of them might be derived either from an increase or from a diminution of a positive quality."

Thomas Young
(1773-1829)



Irvinist Calorific Theories

- (total heat H) = (heat capacity C) $\times$ (absolute temperature T)
- *latent heat* = heat required to keep T constant when C increases.

- *Suppose*: C increases by ΔC at constant T.
- *Then*: H must increase by $\Delta H = \Delta CT$, where ΔH = latent heat.
- *So*: To find absolute zero, measure latent heat for known changes in heat capacity (as measured by specific heat).

- Irvine's result for water and ice: -900°F.
- *But*: Lavoisier and Laplace's results: -600°C to $-14{,}000$°C.
  Dalton's results: $-11{,}000$°F to -4000°F.

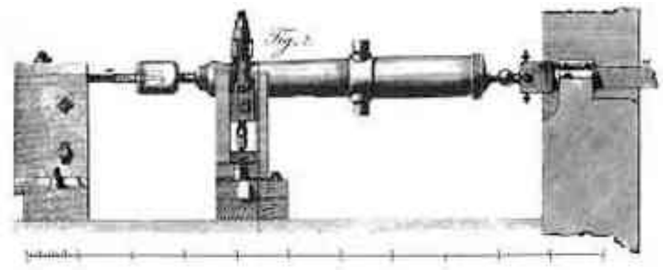
Chemical Calorific Theories

- Temperature = density of free/sensible caloric.
- Latent/combined caloric does not contribute.
- *But*: No way to measure amount of latent caloric in a given body
  - *No way to measure amount of caloric becoming latent or free in a given process.*

Dynamical Theories: Heat = motion of particles

Warning: "...the dynamical theories that were in competition with the caloric theories bore very little resemblance to the dynamical theories that came after thermodynamics" (Chang, pg. 171).

1798. Rumford's Canon-Boring Experiments



- Plunge one end of cannon-borer in box of water.
- Spin borer (horse-powered).

"The result of this beautiful experiment was very striking... At the end of 1 hour I found, by plunging a thermometer into the water in the box...that its temperature had been raised no less than 47 degrees; being now 107° of Fahrenheit's scale... At 2 hours 20 minutes it was at 200°; and at 2 hours 30 minutes it actually boiled! I would be difficult to describe the surprise and astonishment expressed in the countenances of the by-standers, on seeing so large a quantity of cold water heated, and actually made to boil, without any fire." (1798)

Count Rumford
(1753-1814)

• Rumford (1798) "An Inquiry concerning the Source of the Heat Which is Excited by Friction", *Phil. Trans. Roy. Soc. London, 88.*

"...in reasoning on this subject, we must not forget to consider that most remarkable circumstance, that the source of the heat generated by friction, in these experiments, appeared evidently to be *inexhaustible*. It is hardly necessary to add, that any thing which any insulated body, or system of bodies, can continue to furnish without limitation, cannot possibly be a *material substance*: and it appears to me to be extremely difficult, if not quite impossible, to form any distinct idea of any thing capable of being excited, and communicated, in the manner the heat was excited and communicated in these experiments, except it be MOTION." (1798)

"I procured two parallelopipedons of ice, of the temperature of 29°, six inches long, two wide, and two-thirds of an inch thick: they were fastened by wires to two bars of iron. By a peculiar mechanism, their surfaces were placed in contact, and kept in a continued and violent friction for some minutes. They were almost entirely converted into water, which water was collected, and its temperature ascertained to be 35°, after remaining in an atmosphere of a lower temperature for some minutes. The fusion took place only at the plane of contact of the two pieces of ice, and not bodies were in friction but ice. From this experiment it is evident that ice by friction is converted into water, and according to the supposition its capacity is diminished; but it is a well-known fact, that the capacity of water for heat is much greater than that of ice; and ice must have an absolute quantity of heat added to it, before it can be converted into water. Friction consequently does not diminish the capacities of bodies for heat." (1799)

Humphry Davy
(1778-1829)

• Davy (1799) "An Essay on Heat, Light, and the Combinations of Light".

Rumford's Theory (1804).

- *Molecules vibrate around fixed positions (no random motion).*
- *Temperature = frequency of vibrations.*
- *No loss of energy by vibrating molecules, and no absolute zero of temp.*

Bernoulli's Theory (1738).

- *Pressure of a gas is proportional to the vis viva (mv^2) of its molecules.*

Daniel Bernoulli
(1700-1782)

John Herapath's (1790-1868) Theory (1820).

- *Temperature is proportional to velocity of molecules.*

Waterston's Theory (1843).

- *Temperature is proportional to mv^2.*

John Waterston
(1811-1883)

2. Thomson's First Concept of Absolute Temperature.

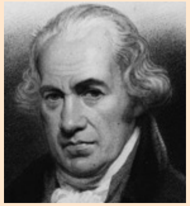
William Thomson (1824-1907)

- Goal: An *absolute* concept of temperature (i.e., *independent of any physical thermometer scale*).

Background (Carnot's Theory of Heat Engines)

- *Heat engine* = any device that generates mechanical work by means of heat

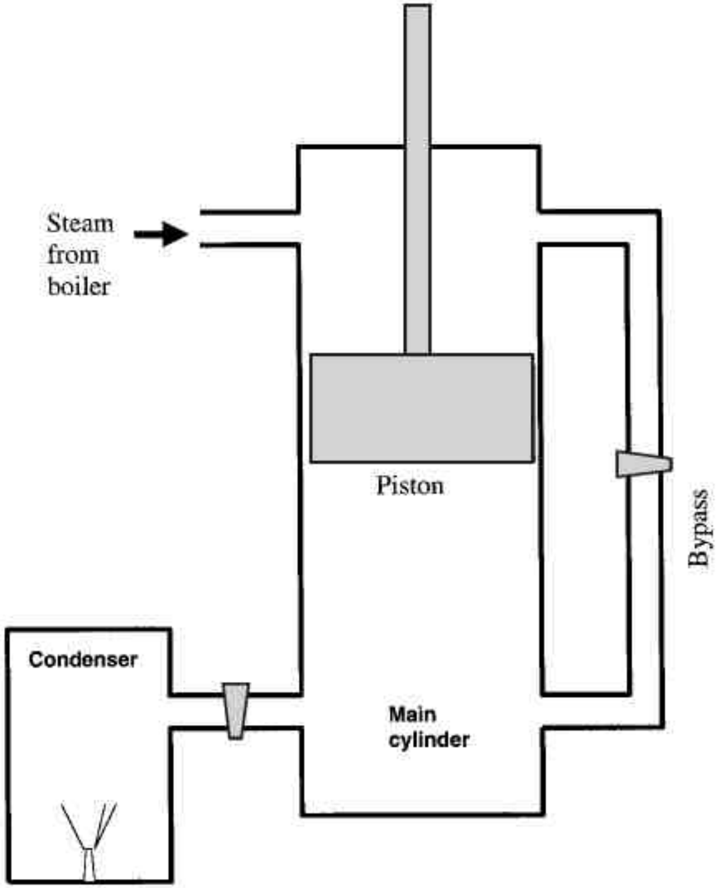
Ex: Steam engine



James Watt (1736-1819)

Two innovations by Watt:

- *Separate condenser*: cold water sprayed into separate condenser, leaving main cylinder at high temp.
- *"Expansive principle"* (1769): Steam introduced into cylinder can do further work by expanding by its own force; so cut off supply from boiler before piston is pushed all the way down.



- Carnot (1824). Abstract heat engine analogous to waterwheel: Heat falls from hot reservoir to cold reservoir and in process performs work.

Sadi Carnot
(1736-1819)

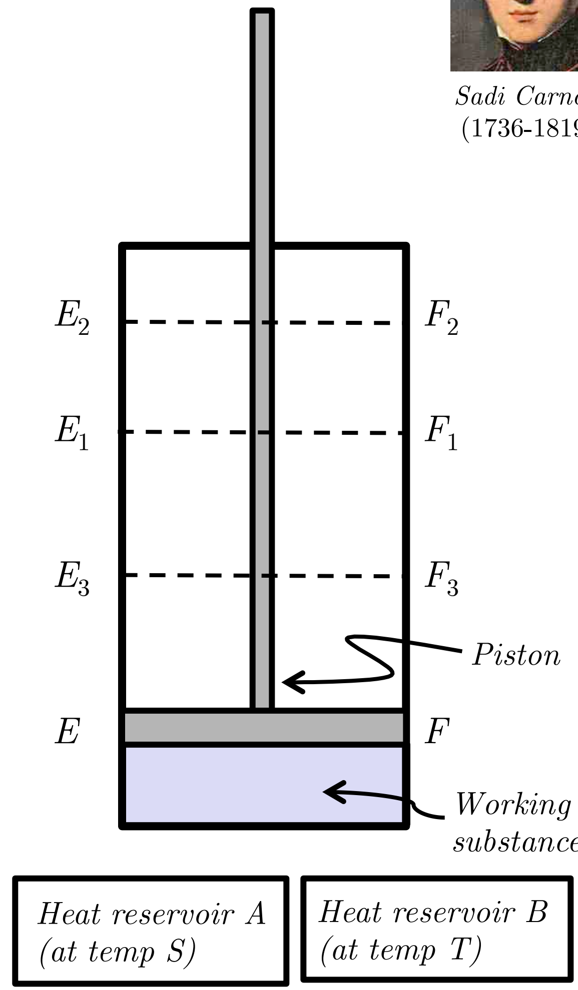
__Carnot cycle:__

1. **Stroke 1.** Working substance at temp S receives heat H from reservoir A, and expands ("*isothermally*"). Piston is pushed up to E_1F_1 and does work W_1.

2. **Stroke 2.** A is removed. Working substance further expands at constant heat ("*adiabatically*"). Temp decreases from S to T. Piston is pushed up further to E_2F_2 doing further work W_2.

3. **Stroke 3.** Working substance is compressed at constant temp T, releasing heat to reservoir B at temp T. Piston is pushed down to E_3F_3, requiring work W_3 performed on working substance.

4. **Stroke 4.** B is removed. Working substance further compresses adiabatically. Piston is pushed back to EF, requiring more work W_4, and temp rises back to S.



- *Efficiency* = (*work performed*)/(*heat absorbed*) = $(W_1 + W_2 - W_3 - W_4)/H$.
- *__Carnot proves__*: efficiency only depends on S and T for "reversible" cycle.

"The characteristic property of the scale which I now propose is, that all degrees have the same value; that is, that a unit of heat descending from a body A at the temperature $T°$ of this scale, to a body B at the temperature $(T-1)°$, would give out the same mechanical effect, whatever be the number T. This may justly be termed an absolute scale, since its characteristic is quite independent of the physical properties of any specific substance"

- *Note*: Not the same notion of "absolute" as in counting temperature from absolute zero.

- Guillaume Amontons (1663-1738): Extrapolate the observed pressure-temperature relation for air until the pressure becomes zero.
  - *Zero pressure = complete absence of heat.*

- *Amontons temperature* (t_a) = air temperature scale with zero point at zero pressure.
  - *Defined in terms of behavior of air.*

Thomson's first absolute temperature T (1848):
1 degree = amount of heat needed to produce one unit of work in a Carnot cycle. (*Independent of any specific substance.*)

3. Thomson's Second Concept of Absolute Temperature.

James Joule
(1818-1889)

- Carnot's theory requires heat to be conserved.
  - *Like water falling in a waterwheel: total in = total out.*

- *Claim (James Joule)*: Heat and work are interconvertible.
  - *In a heat engine, some of the input heat from the hot place is converted into work; the rest is exhausted to the cold place.*

- 1851. Thomson is convinced to reformulate Carnot's theory.

- *Recall*: *Efficiency* = (*work produced*)/(*heat input*) depends only on temperatures of hot and cold reservoirs.
- Thomson writes this as:

$$dW = Q\mu\, dT$$

work produced by a Carnot cycle

heat input

"Carnot's function" = function of temperature.

infinitesimal difference dT between hot and cold reservoirs

- 1854. Collaboration with Joule.

"A more convenient assumption has since been pointed to by Mr. Joule's conjecture, that Carnot's function is equal to the mechanical equivalent of the thermal unit divided by the temperature by the air thermometer [Amonton's termperature t_a]".

- *In other words*: $\mu = J/t_a$

mechanical equivalent of heat

"Carnot's function varies very nearly in the inverse ratio of what has been called 'temperature from the zero of the air-thermometer' [Amontons temperature]... and we may define temperature simply as the reciprocal of Carnot's function".

- *In other words*: $\mu = J/T$

Thomson's absolute temperature

"If any substance whatever, subjected to a perfectly reversible cycle of operations, takes in heat only in a locality kept at a uniform temperature, and emits heat only in another locality kept at a uniform temperature, the temperatures of these localities are proportional to the quantities of heat taken in or emitted at them in a complete cycle of operations."

- *In other words*:

Thomson's second concept of absolute temperature (1854):

$$T_1/T_2 = Q_1/Q_2$$

T_1, T_2 = abs. temps of strokes 1 and 3 of a Carnot cycle.
Q_1, Q_2 = heat absorbed and exhausted in strokes 1 and 3.

Check: Total work for infinitesimal Carnot cycle operating between T and T' with Q, Q' = heat absorbed and exhausted in strokes 1 and 3:

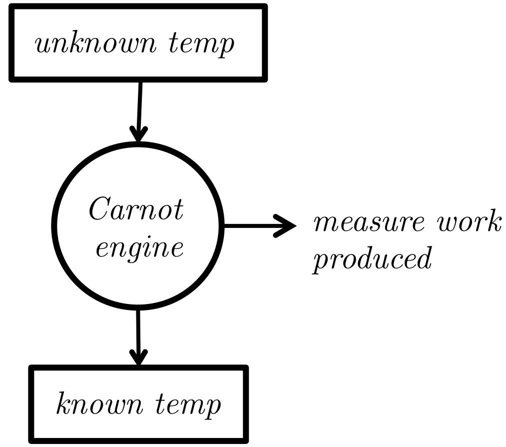
$$\begin{aligned} W &= J(Q - Q') = JQ(1 - T'/T) \qquad \text{since } T/T' = Q/Q' \\ &= JQ(T - T')/T \end{aligned}$$

So: $$\begin{aligned} dW &= JQ(dT/T) \\ &= Q\mu\, dT, \quad \text{just when } \mu = J/T. \end{aligned}$$

4. Operationalizating Absolute Temperature.

A. How to measure Thomson's first absolute temp:

"...take an object whose temperature we would like to measure; use it as a Carnot heat reservoir and run a Carnot engine between that and another reservoir whose temperature is previously known; and measure the amount of mechanical work that is produced, which gives the difference between the two temperatures" (Chang, pg. 187).



- *Problem*: A Carnot engine is perfectly *reversible.*
  - *Absence of friction and other forms of dissipation of heat and work; no transfer of heat across any temperature differences.*

- *Thomson's suggestion*: Use a water-steam system.
  - *Recall*: *Pressure of saturated steam is a function only of temperature.*
  - *Idea*: *Set up correspondence between air-thermometer temperature and absolute temperature using empirical data.*

Total work performed W for heat input H in a water-steam Carnot cycle:

$$W = \int_{p_1}^{p_2} \xi \, dp$$

- *For original Carnot cycle with heat conservation.*
- p_1, p_2 = *const pressures in isothermal strokes 3 and 1.*
- ξ = *difference in volumes at any instant in strokes 2 and 4.*

$$\xi = (1-\sigma)H/k$$

- k = *latent heat per unit volume of steam at a given temp.*
- σ = *ratio of density of steam to density of water.*
- "...the input of heat H produces H/k liters of steam, for which $\sigma H/k$ liters of water needs to be vaporized."

$$W = \int_{p_1}^{p_2} (1-\sigma)(H/k)\, dp$$

$$= H \int_T^S (1-\sigma)(dp/k\, dt)\, dt$$

- t = *air-thermometer temperature.*
- H *is assumed independent of temperature.*

- According to Thomson's first absolute temperature scale, W/H is proportional to $S - T$.
- Can now calculate absolute scale reading for $S - T$ (using above formula) and compare it with actual air-thermometer reading of $S - T$.

$$W/H = \int_T^S (1-\sigma)(dp/k\,dt)\,dt$$

<u>*Problems*</u>:

1. Requires values of k (latent heat/vol.).
   - *Only had experimental values for latent heat/weight.*
   - *Forced Thomson to assume Boyle's law (pv = const.) and Gay-Lussac's law (p/t = const.).*

2. Assumes pressure of saturated steam depends only on temperature.

   > <u>But</u>: "We should also keep in mind that his use of the pressure-temperature relation was not in the definition of absolute temperature, but only in its operationalization" (Chang, pg. 190).

3. How is heat to be measured?
   - <u>*Assumption:*</u> *it is independent of air-thermometer temperature.)*

Air-thermometer temperature	Absolute temp (first definition)
0°C	0
5	5.660
10	11.243
15	16.751
20	22.184
25	32.834
30	38.053
35	43.201
40	48.280
45	53.291
50	58.234
55	63.112
60	67.925
65	72.676
70	77.367
75	82.000
80	86.579
85	91.104
90	95.577
100	100
150	141.875
200	180.442
231	203.125

(Chang, pg. 190)

B. How to measure Thomson's second absolute temperature:

- ***Claim***: An ideal gas thermometer gives the absolute temperature exactly.

Consider: Work W_i done by isothermal expansion of ideal gas ($pv = ct_a$).

$$W_i = \int_{v_0}^{v_1} p\,dv = \int_{v_0}^{v_1} (ct_a/v)\,dv = ct_a \log(v_1/v_0)$$

$$\partial W_i/\partial t_a = c\log(v_1/v_0) = W_i/t_a$$

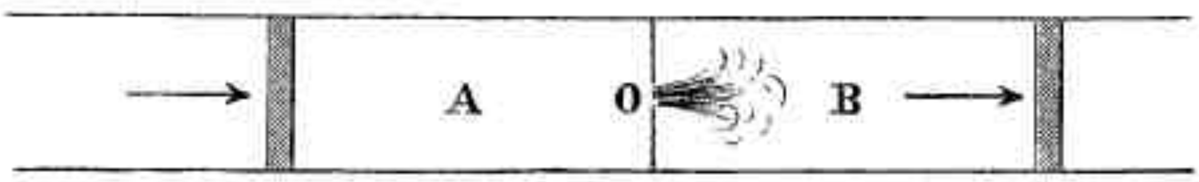
- ***Note***: $dW_i = Q\mu\,dT = (\partial W_i/\partial T)\,dT$.
- ***So***: $\partial W_i/\partial T = Q\mu = JQ/T$ (where $\mu = J/T$).
- ***So***: Amontons temp (t_a) of an ideal gas behaves like abs. temp. (T) just when $JQ = W_i$!

What $JQ = W_i$ means:

- ***Mayer's Hypothesis***: All the heat absorbed in an isothermal expansion of an ideal gas gets converted into mechanical energy.
- ***So***: If Mayer's Hypothesis is correct, then an ideal gas thermometer measures absolute temp.

Julius Robert Mayer
(1814-1878)

How to test Mayer's Hypothesis: The Joule-Thomson Experiment



- Let gas flow through a narrow opening.
  - *- Isothermal for an ideal gas; actual gas should cool.*

- Joule and Thomson's formula for an actual gas:

$$v = CT/p - (1/3)AJK(273.7/T)^2$$

T = abs. temp; v = volume; p = pressure
K = specific heat
A = constant characterizing type of gas
J = mechanical equivalent of heat
C = parameter indepenent of v and t

- Allows T to be calculated in terms of empirical data on actual gases.

Abs temp (2nd def) minus 273.7	Air-thermometer temperature
0	0
20	20 + 0.0298
40	40 + 0.0403
60	60 + 0.0366
80	80 + 0.0223
100	100
120	120 – 0.0284
140	140 – 0.0615
160	160 – 0.0983
180	180 – 0.1382
200	200 – 0.1796
220	220 – 0.2232
240	240 – 0.2663
260	260 – 0.3141
280	280 – 0.3610
300	300 – 0.4085

(Chang, pg. 196)

5. Operationalization.

- <u>*Can we take operationalization for granted?*</u>

  "If we possess any thermodynamic relation, or any equation involving τ [absolute temperature] and other quantities which can be expressed in terms of p [pressure] and v [volume], then each such relation furnishes a means of estimating τ when the other quantities are known." (Preston 1904.)

- <u>*But*</u>: The p and v that occur in thermodynamics are *abstract concepts*.

<u>*Example: pressure*</u>.

- "...there is no reason to assume that the mercury manometer was any more straightforward to establish than the mercury thermometer."
- In thermodynamics, pressure is universally applied to microscopic, and perfectly reversible processes; as well as infinitesimal processes.
- In the kinetic theory of gases, pressure = collective impact of countless gas molecules.

- *Abstraction*

> "the act of removing certain properties from the description of an entity; the result is a conception that can correspond to actual entities but cannot be a full description of them."

- *Different from idealization*:

> "...the geometric triangle is an abstract representation of actual triangular objects, deprived of all qualities except for their form. (A triangle is also an idealization by virtue of having perfectly straight lines, lines with no width, *etc.*)"

Abstract concepts:
- Carnot cycle.
- ideal gas.
- absolute temperature.

- Operationalization involves taking an abstract concept that cannot itself possess concrete values, and finding an actual physical system corresponding to it that can.

Two Steps in Operationalization

1. *Imaging*: Finding a concrete image of the abstract system that defines the abstract concept.
   - *Abstract system* = Carnot cycle.
   - *Concrete image* = frictionless cylinder-and-piston system filled with a water-steam mixture that is heated and cooled by reservoirs of infinite capacity.
2. *Matching*: Finding an actual physical system that matches the image.
   - *If no such matching can be done, the image is deemed to be idealized.*

"An unoperationalized abstract concept does not correspond to anything definite in the realm of physical operations, which is where values of physical quantities belong." (Chang, pg. 207.)

But: "...how can the question of validity enter the process of operationalization?

Response: "The answer has to lie in looking at the correspondence between systems, not between the real and measured values of a particular quantity. A valid operationalization consists in a good correspondence between the abstract system and its concrete image, and between the concrete image and some system of actual objects and operations."

Thomson's strategy for operationalizing first absolute temperature

- *Abstract system*: Carnot cycle.
- *Problem*: Reversibility
  - *Frictionless pistons; perfect insulation; all heat transfer must occur between objects with equal temperatures).*
- *Solution*: Only consider isothermal expansion.
  - *Find a concrete image of just the first stroke of a Carnot cycle, rather than the whole cycle (steam-water system).*

Thomson's strategy for operationalizing second absolute temperature

- *Abstract system*: ideal gas.
- *Problem*: No exact match between image of ideal gas thermometer and the collection of all actual thermometers.

  > "...the image stipulated only one temperature value in each situation, and the collection of the gas thermometers returned multiple values."

- *Solution*: Joule-Thomson experiment provided empirical means of correcting actual gas thermometers to approximate absolute temperature.

6. Accuracy Through Iteration.

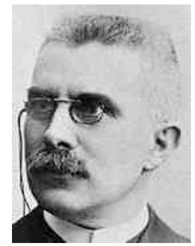
"...there are no pre-existing values of abstract concepts that we can try to approach... the 'real' values only come into being as a result of a successful operationalization." (Chang, pg. 213.)

Hugh Callendar
(1863-1930)

Callendar-Le Chatelier (1887)

- *Assume*: Air-thermometer temp (t_a) and abs temp (T) are very close.
- *Then*: Actual gas law is given by:

$$pv = (1-\phi)RT \qquad \begin{array}{l} R = \text{const; } T = \text{abs. temp} \\ \phi = \text{function of } T \text{ and } p \end{array}$$



Henri Louis Le Chatelier
(1850-1936)

- *Now*: Estimate ϕ using results of Joule-Thomson experiment:

$$\phi = 0.001173(p/p_0)(T_0/T)^3 \qquad \begin{array}{l} p_0 = \text{standard pressure} \\ T_0 = \text{abs temp of melting ice} \end{array}$$

- This *empirical* estimation substitutes T for t_a.

Isn't this circular? "This is allowed, as an approximation, on the assumption that T and t_a are roughly equal because ϕ is very small."

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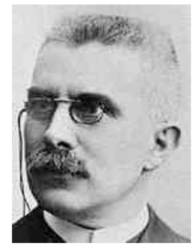

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p_0 = standard pressure
T_0 = abs temp of melting ice

- *Now*: Substitute estimated ϕ back into actual gas law, and recalibrate air thermometer to adjusted law.
- As more and more such corrections are done, air thermometer reading approaches absolute temperature.

- In principle, can't rest with a single correction, even if it's very small (as Joule and Thomson did):
  - *For each gas, need to see whether corrections actually get smaller.*
  - *Need to demonstrate such convergence for all gas thermometers (abs. temp should be independent of any physical thermometer scale).*

<u>*What Operationalism suggests about justification:*</u>

> "... in an iterative process, point-by-point justification of each and every step is neither possible nor necessary; what matters is that each stage leads on to the next one with some improvements... [so] it makes sense to relax the sort of demand for justification that can lead us to seek illusory rigor." (Chang, pg. 215.)