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Historical Studies in the Physical and Biological Sciences

HASOK CHANG*

Spirit, air, and quicksilver: The search for the “real” scale of temperature

The thermometer, as it is at present construed, cannot be applied to point out the exact proportion of heat....It is indeed generally thought that equal divisions of its scale represent equal tensions of caloric; but this opinion is not founded on any well decided fact.

Joseph-Louis Gay-Lussac, 1802¹

HOW CAN WE trust our measuring instruments? This has been a persistent question for practicing scientists as well as historians, philosophers, and sociologists of science. Much nervous discussion has revolved around complex and spectacular instruments (bubble chambers, electron microscopes, solar-neutrino detectors, gravitational-wave detectors, etc.).² The question is a relevant and vexing one even for apparently pedestrian pieces of machinery, for which the conceptual and philosophical issues can be exposed much more clearly in fact.

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The following abbreviations are used: *JNP*, *Journal of natural philosophy, chemistry, and the arts*; *MAS*, Académie des sciences, Paris, *Mémoires*; *PT*, Royal Society of London, *Philosophical transactions*.

1. Joseph-Louis Gay-Lussac, “Enquiries concerning the dilatation of the gases and vapors,” *JNP*, 3 (1802), 207-216, 257-267, on 208; originally published as “Sur la dilation des gaz et des vapeurs,” *Annales de chimie*, 43 (1802), 137-175.

2. E.g., Peter Galison, *How experiments end* (Chicago, 1987); Nicolas Rasmussen, “Facts, artifacts, and mesosomes: Practicing epistemology with the electron microscope,” *Studies in history and philosophy of science*, 24 (1993), 227-265; Dudley Shapere, “The concept of observation in science and philosophy,” *Philosophy of science*, 49 (1982), 485-525; and Harry Collins, *Changing order* (London, 1985).

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In his *Elementa chemiae*, the enormously influential textbook of chemistry first published in 1732, Herman Boerhaave reported that he had asked “that industrious and incomparable Artist, Daniel Gabriel Fahrenheit, to make me a couple of Thermometers, one with the densest of all Fluids, Mercury, the other with the rarest, Alcohol, which should be so nicely adjusted, that the ascents of the included liquor in the same degree of Heat, should be always exactly equal in both.” The two thermometers did not quite agree with each other. Fahrenheit was at a loss for an explanation, since he had graduated them in exactly the same way. In the end he attributed the problem to the fact that he had not made the instruments with the same glass. Apparently that “the various sorts of Glass made in Bohemia, England, and Holland, were not expanded in the same manner by the same degree of Heat.” Boerhaave accepted this explanation.³

But it was soon clear that differences in the working fluid also caused discrepancies. By 1739 at the latest, R.A.F. de Réaumur had noticed that mercury and alcohol thermometers did not read the same throughout their common range. He blamed the discrepancy on differences in the rate of expansion of the two liquids.⁴ Réaumur’s observation and explanation were soon accepted.⁵ It is not a subtle effect, as the following table shows:

Table 1. Comparison of thermometers (in degrees centigrade)^a

Mercury	Alcohol	Water
0	0	0
25	22	5
50	44	26
75	70	57
100	100	100

a. Gabriel Lamé, *Cours de physique de l'École Polytechnique* (Paris, 1836), 208.

An operationalist like Percy Bridgman would say that each type of instrument defines a separate concept, so there is no reason for us to expect or insist on agreement among different types.⁶ A conventionalist might say that we can choose one instrument as the standard and make the others incorrect by definition. As Réaumur put it, it is possible to calibrate an alcohol thermometer on the standard of a mer-

3. Herman Boerhaave, *Elements of chemistry*, trans. Timothy Dallowe (London, 1735), 87; *Elementa chemiae* (Leyden, 1732), 141. Other recipients of Fahrenheit’s thermometers also noted discrepancies which could be as large as 6° at 96° on his scale. Pieter van der Star, ed. and trans., *Fahrenheit’s letters to Leibniz and Boerhaave* (Leyden, 1983), 147, 149, 161, 163.

4. René Antoine Ferchault de Réaumur, “Observations du thermomètre pendant l’année M.DCCXXXIX, faites à Paris et en différent pays,” *MAS*, 1739, 447-466, on 462.

5. W.E. Knowles Middleton, *A history of the thermometer and its use in meteorology* (Baltimore, 1966), 124.

6. Percy Bridgman, *The logic of modern physics* (New York, 1927), esp. 3-9.

cury thermometer "when one wishes the alcohol thermometer to speak the language of the mercury thermometer," and vice versa.⁷ A more sophisticated conventionalist like Henri Poincaré would prefer the temperature standard that makes the laws of thermal phenomena as simple as possible.

Very few scientists making or using thermometers took any of those philosophical positions. Most were realists in the sense that they believed in the existence of an objective property called temperature and wanted to know how to measure its true values. If various thermometers disagreed in their readings, then no more than one of them could be right. The question, which thermometer gave the "real temperature" or the "real degree of heat" is a more profound and difficult one than might at first appear.

By the middle of the 18th century, the accepted method of graduating thermometers was the "two-point method." The centigrade scale takes the freezing and boiling points of water as the fixed points. We mark the height of the thermometric fluid at freezing 0°, that at boiling 100°; then we divide up the interval equally, so that it reads 50° half-way up and so on. The procedure operates on the assumption that the net expansion of glass plus fluid is uniform with temperature. To check this assumption, we need to make an experimental plot of volume vs. temperature. But there is the rub: we need a thermometer, which is the very thing we are trying to create, to measure the temperature.

Whenever a method of measurement rests on an empirical law, we have the same kind of problem in testing and justifying that law. This may be called the "problem of nomic measurement."⁸ To put the problem precisely and abstractly:

- (1) We want to measure quantity X .
- (2) Quantity X is not directly observable by unaided human perception so we infer it from another quantity Y , which is directly observable.⁹
- (3) For this inference we need a law that expresses X as a function of Y , $X = f(Y)$.
- (4) The form of this function f cannot be discovered or tested empirically, because that would involve knowing the values of both Y and X , and X is the unknown variable that we are trying to measure.

This circularity is probably the most crippling form of the theory-ladenness of observation.

7. R.A. Réaumur (ref. 4), 462: "lorsqu' on voudra que le Thermomètre à esprit de vin parle la langue de celui à mercure."

8. Hasok Chang, "Circularity and reliability in measurement," *Perspectives on science*, 3 (1995), 153-172, esp. 153-154.

9. I adopt the concept of observability in Bas C. van Fraassen, *The scientific image* (Oxford, 1980), 13-19. Temperature is observable only in a very limited range of values and with little precision.

This paper discusses the practical solution of one small example of this fundamental philosophical puzzle: the choice of the right thermometric fluid from among the bewildering variety of substances tried. These included mercury, ether, alcohol, atmospheric air, sulfuric acid, linseed oil, water, salt water, olive oil, petroleum, and lumps of clay.

Only three of these known fluids became significant contenders for the claim of indicating true temperatures: atmospheric air, mercury, and ethyl alcohol, often referred to as “spirit of wine” or simply “spirit.” The paper ends with the establishment of the air thermometer as the best standard in the 1840s.

2. THE METHOD OF MIXTURES

Earlier versions

Thermometry began with no firm principles regarding the choice of thermometric substances.¹⁰ The very first thermometers of the early 17th century used air. Those fickle instruments were replaced by “liquid-in-glass” thermometers, for which the preferred liquid for some time was spirit. Fahrenheit, working in Amsterdam, established the use of mercury during the 1710s; small, neat, and reliable, his mercury thermometers gained currency in the rest of Europe partly through physicians trained in Holland.¹¹ Réaumur preferred spirit and made spirit thermometers popular in France. Elsewhere mercury came to be preferred by most people including Anders Celsius (1701-1744), inventor of the centigrade scale.

Initially people assumed that the thermometric fluid they used expanded uniformly with increasing temperature. After observation of the disagreement between different types of thermometers, people modified the assumption to the assertion that one or another fluid expanded uniformly and others did not.¹² The battle pitted not only liquids and gases against one another, but both against solids, which, according to Thomas Young, expanded more regularly than either.¹³ Jacques Barthélemy Micheli du Crest, a Swiss military engineer who spent much of his life in political exile and in prison, published an idiosyncratic argument in 1741 to show that spirit expanded more regularly than mercury.¹⁴ However, his contempo-

10. For the early history, see Henry Carrington Bolton, *The evolution of the thermometer, 1592-1743* (Easton, 1900), and Middleton (ref. 5).

11. *Encyclopaedia britannica, supplement* (1824), 5, 331.

12. Jean-André De Luc, *Recherches sur les modifications de l'atmosphère* (2 vols., Geneva, 1772), 1, 290: “C'est précisément la disparité des marches de l'esprit-de-vin & du mercure, qui montrant certainement que l'une ou l'autre n'est pas d'accord avec la chaleur, les avoit rendus suspects l'une & l'autre à M. le Sage.”

13. Thomas Young, *Lectures on natural philosophy and the mechanical arts*, ed. P. Kelland (London, 1845), 493; originally published in 1807. “The expansion of solids probably approaches the nearest to the steps of the natural scale, although even in this there seems to be some inequality; but that of mercury is scarcely less regular” (ibid., 497).

14. Micheli du Crest took the supposedly constant temperature of deep cellars and mines as a fundamental fixed point of thermometry, and expected the most extreme temperatures ob-

rary George Martine, a Scottish physician, insisted that "[spirit] does not condense very regularly" in strong colds, and plumped for the mercury thermometer.¹⁵ Johann Heinrich Lambert also claimed that the expansion of spirit was irregular. He believed, with Guillaume Amontons, that air expanded uniformly and liquids did not. Neither Amontons nor Lambert, however, gave adequate arguments in support of that assumption.¹⁶

Before the caloric theory there was only one tradition of cogent reasoning and experimentation with a potential to settle the argument. This was the method of mixtures. Mix equal amounts of freezing water (at 0° centigrade, by definition) and boiling water (at 100°, again by definition) in an insulated vessel; if a thermometer inserted in the mixture reads 50°, it indicates the real temperature. Such mixtures could be made in various proportions (1 part boiling water and 9 parts freezing water should give 10° centigrade, and so on), to test thermometers for correctness everywhere on the scale between the two fixed points.

The earliest generally recognized employment of the method of mixtures occurs in the work of Carlo Renaldini, then, in 1694, Professor of Mathematics at Padua, and once a member of the Accademia del Cimento in Florence. Renaldini graduated his spirit thermometer in 12 divisions by mixing measured proportions of boiling water and ice-cold water, believing that the proportions gave indications of absolute degrees of heat.¹⁷ The first attempt to use mixtures for *testing* thermometers graduated by other methods was probably made by Brook Taylor, Secretary of the Royal Society of London from 1714 to 1718, who thus tested the linseed oil thermometer in 1723. It passed.¹⁸ Taylor's test was not a very precise one and he gave no numbers. In 1760, Joseph Black revived the method of mixtures and obtained satisfactory results on the mercury thermometer.¹⁹

served on the surface (in Senegal and Kamchaka) would be equally distant from this middle point. His spirit thermometers gave readings more in accord with that hypothesis, than did his mercury thermometers. See Middleton (ref. 5), 90-91; De Luc (ref. 12), 329; and Johann Carl Fischer, *Physikalisches wörterbuch* (8 vols., Göttingen, 1798-1808), 5 (1804), 76-77.

15. George Martine, *Essays and observations on the construction and graduation of thermometers*, 2nd edn. (Edinburgh, 1772), 26 (text of 1738).

16. Johann Heinrich Lambert, *Pyrometrie, oder vom Maaße des Feuers und der Wärme* (Berlin, 1779), 78; Guillaume Amontons, "Discours sur quelques propriétés de l'air, & le moyen d'en connoître la temperature dans tous les climats de la terre," *MAS*, 1702, 155-174.

17. Carlo Renaldini, *Naturalis philosophia* (Patavii, 1694), 275-276. Cf. De Luc (ref. 12), 286-288, and Middleton (ref. 5), 55-56.

18. Brook Taylor, "An account of an experiment, made to ascertain the proportion of the expansion of the liquor in the thermometer, with regard to the degrees of heat," *PT*, 32 (1722-23), 291. By this time Fahrenheit was using the method of mixtures to check the accuracy of his thermometers; Van der Star (ref. 3), 163.

19. Joseph Black, *An enquiry into the general effects of heat; with observations on the theories of mixture* (London, 1770), 8-12, and *Lectures on the elements of chemistry*, ed. John Robison (2 vols., London, 1803), I, 56-59. Black states that when he carried out his experiments, motivated by some reflections about fluidity and its temperature dependence, he did not know that anyone else had done the same kind of work. See also Robison's

De Luc's contributions

The person who brought the tradition of mixtures to its culmination was Jean André De Luc. The elder son of a radical clockmaker who was friendly with Jean-Jacques Rousseau, De Luc maintained equally active interests in science, commerce, politics, and religion. He advanced natural theological explanations of geological findings, arguments against Lavoisier's new chemistry, and a controversial theory of rain postulating the transmutation of air into water.²⁰ De Luc's pioneering excursions into the Alps stimulated and integrated his scientific interests in natural history, geology, and meteorology. His decisive improvement of the method of measuring the heights of mountains by barometric pressure made him one of the most important physicists in Europe.²¹ More generally he was famous for his inventions and improvements of meteorological instruments, and for the keen observations he made with them.

Shortly after the publication of his first major scientific work in 1772, the two-volume *Recherches sur les modifications de l'atmosphère*, De Luc's business collapsed and he retired from commercial life and devoted himself entirely to scientific work. In 1773 he settled in England, where he was welcomed as a Fellow of the Royal Society, and served on its committee on thermometry chaired by Henry Cavendish. He enjoyed the position of "Reader" to Queen Charlotte. He based himself to his dying day in the court of George III, although he continued to travel and kept up his scientific connections particularly with the Lunar Society of Birmingham and the University of Göttingen, where he was titular professor of geology.²²

Perfectionism had delayed the publication of the *Recherches* for ten years, though something of its content was widely known and highly regarded through a draft submitted to the Paris Academy of Sciences. Readers found in the book not only the anxiously awaited discussion of barometric hypsometry, but also a detailed discourse on the construction and employment of thermometers. De Luc had come to thermometers because of the necessity to correct barometer readings for variations in temperature.²³ De Luc observed that the choice of thermometric fluid was just that—a matter of choice. However, he insisted that there be some principle guiding the choice. The "fundamental principle" for him was that the

preface to Black, *Lectures*, I, xxxix-xl; Thomas Thomson, *An outline of the sciences of heat and electricity* (London, 1830), 45-46; and Arthur L. Donovan, *Philosophical chemistry in the Scottish enlightenment: The doctrines and discoveries of William Cullen and Joseph Black* (Edinburgh, 1975), 231-235.

20. W.E. Knowles Middleton, "Chemistry and meteorology, 1700-1825," *Annals of science*, 20 (1964), 125-141.

21. Theodore S. Feldman, "Applied mathematics and the quantification of experimental physics: The example of barometric hypsometry," *HSPS*, 15:2 (1985), 127-197.

22. Albert De Montet, *Dictionnaire biographique des Genevois et des Vaudois* (Lausanne, 1878), 2, 79-82;

23. De Luc (ref. 12), 219-221.

fluid "must measure equal variations of heat by equal variations of its volume."²⁴ But which fluid, if any, actually satisfied this requirement had not been established.

De Luc's investigations resulted in the conclusion that mercury was the most satisfactory thermometric liquid.²⁵ What he regarded as the "direct proof" of mercury's superiority was the result of mixing experiments.²⁶ He attributed the method of mixtures primarily to his mentor and friend George-Louis Le Sage the Younger, whose explanations of gravity as a result of bombardment by fast small particles would have a decisive influence on Pierre Prevost's theory of radiant heat. De Luc mixed two samples of water at previously known temperatures and compared the reading given by a thermometer with the calculated temperature.²⁷ The verdict was unequivocal. The mercury thermometer deviated from degrees of real heat by very little, as shown in Table 2.

Table 2. Results of De Luc's test of the mercury thermometer by the method of mixtures^a

	degree of real heat	mercury thermometer reading ^b	condensation of mercury between last two points
boiling water	z + 80	80.0	-
	z + 75	74.7	5.3
	z + 70	69.4	5.3
	z + 65	64.2	5.2
	z + 60	59.0	5.2
	z + 55	53.8	5.2
	z + 50	48.7	5.1
	z + 45	43.6	5.1
	z + 40	38.6	5.0
	z + 35	33.6	5.0
	z + 30	28.7	4.9
	z + 25	23.8	4.9
	z + 20	18.9	4.9
	z + 15	14.1	4.8
	z + 10	9.3	4.8
melting ice	z + 5	4.6	4.7
	z	0.0	4.6

a. De Luc (ref. 12), I, 301.

b. In degrees Réaumur (freezing=0°, boiling=80°).

24. Ibid., 222-223.

25. He dismissed solids and gave many detailed reasons against air, with particular reference to Amontons's air thermometer (ibid., 275-283).

26. Ibid., 285.

27. De Luc did not use boiling water "because it could neither be measured or weighed" (ibid., 292), or freezing point water because it could not be prepared in sufficient quantity (ibid., 298-299). So he used water that was only nearly boiling and nearly freezing. This might seem to saddle De Luc with a vicious circularity, since he had to use a thermometer to

Even more decisive than this consideration of mercury alone was the comparative view. From De Luc's results juxtaposing the performance of 8 different liquids, shown in Table 3, there was no question that mercury gave the best available approximation to the “real” degrees of heat.

Table 3. De Luc's comparison of the readings of various thermometers with the real degree of heat^a

real degree of heat	40.0
mercury thermometer	38.6
olive oil thermometer	37.8
camomile oil thermometer	37.2
thyme oil thermometer	37.0
saturated salt water thermometer	34.9
spirit thermometer	33.7
water thermometer	19.2

a. De Luc (ref. 12), I, 311.

These results agreed with De Luc's theoretical notion that the condensation of liquids proceeded uniformly according to temperature until contraction so crowded the molecules that they resisted further condensation. He inferred that a significant slowing down of condensation indicated that the liquid had entered the crowded phase. It followed that, “the liquid whose rate of condensation increases in comparison to that of all other liquids is very probably the one in which differences of volume are closest to being proportional to differences of heat.” On this criterion, too, mercury was shown to be the best choice. De Luc awarded mercury “an *exclusive* preference” in the construction of the thermometer; “nature gave us this mineral for making thermometers!”²⁸

De Luc's experiments and arguments in favor of mercury gained wide acceptance. Horace-Bénédict de Saussure, De Luc's most prominent rival, disputed with him over the construction of hygrometers and the cause of the cold that prevails on mountain-tops; but when it came to thermometry, Saussure, who had been close to the spiritist Micheli du Crest, followed De Luc. When Saussure and Marc-Auguste Pictet undertook to measure the temperature at the depth of Lake Geneva in 1779, they used two thermometers that Saussure had inherited from Micheli carefully recalibrated according to De Luc's instructions. For Saussure, De Luc's mercury thermometer was the “common thermometer.”²⁹ A decade later Pictet again ex-

measure the temperatures of his hot and cold waters. He had a process of correction that satisfied him (ibid., 299-306), but the basic procedure is not problematic if it is viewed as a test of consistency. If the mercury thermometer is correct, and we mix equal amounts of water at temperatures a° and b° as measured by it, then the mercury thermometer should give $(a+b)/2^{\circ}$ for the temperature of the mixture.

28. Ibid., 284-285, 330.

29. Douglas Freshfield, *Life of Horace Benedict de Saussure* (London, 1920), 440, 352;

pressed his approval of the choice of mercury as the substance best indicating the gradations of fire, though he did not make an explicit reference to De Luc there.³⁰

In France as well as Geneva De Luc's mercury thermometers became standard, though under the name of Réaumur. Support could not have come from any more authoritative sources than Antoine-Laurent Lavoisier and Pierre-Simon Laplace, who supported their choice of the mercury thermometer by reference to De Luc's experiments.³¹ Laplace later revised his opinion, but Lavoisier seems to have maintained his trust in mercury and in De Luc's reasoning.³² After Lavoisier's death fresh advocacy came in the authoritative *Traité élémentaire de physique* (1803) by René-Just Haüy, a textbook commissioned by Napoleon for use in the newly established *lycées*, and soon a recommended text for the *Ecole Polytechnique* as well. Thus it was with Napoleon's authority as well as his own that Haüy stated: "The experiments of De Luc have served...to render evident the advantage possessed by mercury, of being amongst all known liquids, that which approaches the most to the state of undergoing dilatations exactly proportional to the augmentations of heat, at least between zero and the degrees of boiling water."³³

In Britain the community of chemists educated by Black endorsed the use of mercury thermometers, citing both Black and De Luc. The most influential of them was Thomas Thomson, Professor of Chemistry in Glasgow.³⁴ The support for De Luc's work cut across the controversy surrounding the doctrine of heat capacity advanced by William Irvine, also a student and successor of Black in Glasgow. Although Irvine's views on the matter are not clear, the Irish physician Adair Crawford, the Glasgow lecturer of chemistry John Murray, and Irvine's own son (in introductory papers to the posthumous edition of his father's works), voiced unequivocal support for De Luc.³⁵ The third edition of the *Encyclopaedia britannica*

H.B. de Saussure, *Voyages dans les alpes* (2 vols., Neuchatel, 1779-86), 1, 21-24, 2, chapt. 35. Saussure noted that De Luc, not Réaumur, devised the 80° thermometer. Réaumur had used alcohol and had graduated his thermometers using only one fixed point.

30. Mark Augustus Pictet, *An essay on fire*, trans. W. B[elcome] (London, 1791), 9; originally published as *Essai sur le feu* (Geneva, 1790).

31. Antoine-Laurent Lavoisier and Pierre-Simon Laplace, *Mémoire sur la chaleur* (Paris, 1920), 14-15 (text of 1783).

32. E.g., *Oeuvres*, 2 (Paris, 1862), 729, 776.

33. Alfred Lacroix, "La vie et l'oeuvre de l'Abbé René-Just Haüy," Société Française de Minéralogie, *Bulletin*, 67 (1944), 15-226, on 50-54, 154-156; A. Fourey, *Histoire de l'Ecole Polytechnique* (Paris, 1828), 257; René Just Haüy, *An elementary treatise on natural philosophy*, trans. Olinthus Gregory (2 vols., London, 1807), 1, 142; originally published as *Traité élémentaire de physique* (Paris, 1803). Haüy argued against the air thermometer in the same manner as De Luc (ref. 12), 259-260.

34. Thomas Thomson, *A system of chemistry* (4 vols., Edinburgh, 1802), 1, 273-276.

35. Adair Crawford, *Experiments and observations on animal heat, and the inflammation of combustible bodies* (London, 1779), 5-7, 119-120; and *Experiments and observations on animal heat, and the inflammation of combustible bodies*, 2nd edn. (London, 1788), 18f; John Murray, *Elements of chemistry* (2 vols., Edinburgh., 1801), 1, 73-77, and *A system of chemistry*, 4th edn. (4 vols., Edinburgh, 1819), 1, 217-218; Willima Irvine and William

(1797), a good source for Scottish opinion, cited De Luc as the authority for the view that the mercury thermometer indicated the real degree of heat.³⁶

Crawford's personal influence extended to England since he worked in London. In the two editions (1779, 1788) of his famous and controversial Irvinist treatise on animal heat Crawford endorsed De Luc's results, on the basis of his own repetition of the experiments. William Henry, John Dalton's colleague in Manchester, credited Crawford with establishing the uniformity of mercury's expansion by the method of mixtures. This was in his *Epitome of chemistry*, first published in 1801, "the most popular and successful chemistry text in England for more than 30 years."³⁷ Support also came from William Nicholson, founder and editor of the *Journal of natural philosophy, chemistry, and the arts*, and author of an important textbook on natural philosophy.³⁸ Tiberius Cavallo followed suit, in his *Elements of natural or experimental philosophy* of 1803.³⁹ To make an end of the evidence for the popularity of De Luc's argument for mercury's near-uniform expansion in England, both the encyclopedic applied mathematician Charles Hutton and Humphry Davy's successor at the Royal Institution William Brande promoted it.⁴⁰

De Luc's argument also found favor in Germany. The fourth volume (1791) of the monumental *Physikalisches Wörterbuch* by Johann Gehler gave a detailed and approving discussion of the advantages of mercury and cited De Luc often.⁴¹ Friedrich Gren, Professor of Physics and Chemistry in Halle, the founder-editor of the *Journal* (later *Annalen*) *der Physik*, and Johann Carl Fischer, professor and historian of physics, advocated and defended De Luc's thermometry.⁴² Fischer ascribed great importance to De Luc's work; the index of his *Geschichte der Physik* (1801-1808) has far more references to De Luc than to Lavoisier or Laplace, almost as many as to Newton. De Luc's position was also championed in the impor-

Irvine, *Essays chiefly on chemical subjects* (London, 1805), 43.

36. *Encyclopaedia britannica*, 3rd edn., 18 (1797), 494.

37. E.L. Scott's entry on Henry in the *Dictionary of scientific biography*, 6, 284; William Henry, *An epitome of chemistry* (London, 1801), 8, in later editions entitled *The elements of experimental chemistry*. The French translation was used as a textbook in the *Ecole Polytechnique* in 1812-13, according to Fourcy (ref. 33), 277.

38. William Nicholson, *An introduction to natural philosophy*, 2nd edn. (2 vols., London, 1787), 2, 75; A.F. Fourcroy, *Elements of chemistry and natural history (To which is prefixed, the Philosophy of chemistry)*, 5th edn., trans. William Nicholson, ed. John Thomson (3 vols., Edinburgh, 1800), 1, 145.

39. Tiberius Cavallo, *The elements of natural or experimental philosophy* (4 vols., London, 1803), 3, 26-30.

40. Charles Hutton, *A philosophical and mathematical dictionary*, new edn. (2 vols., London, 1815), 1, 506-507; William Thomas Brande, *A manual of chemistry* (London, 1819), 25.

41. Johann Samuel Traugott Gehler, *Physikalisches Wörterbuch* (5 vols., Leipzig, 1787-95), 4 (1791), 326-335.

42. Friedrich Albrecht Carl Gren, *Grundriß der Naturlehre in seinem mathematischen und chemischen Theile neu bearbeitet* (Halle, 1793), 499-500; J.C. Fischer (ref. 14), 73-79; Johann Carl Fischer, *Geschichte der Physik seit der Wiederherstellung der Künste und Wissenschaften bis auf die neuesten Zeiten* (8 vols., Göttingen, 1801-1808), 5 (1804), 21f.

tant textbook by Ernst Gottfried Fischer. Fischer credited De Luc for the choice of mercury and followed Saussure in calling the mercury thermometer on an 80-degree scale with boiling and freezing of water as fixed points "De Luc's thermometer."⁴³ In the realm of practice, Johann Jakob Hemmer, who coordinated the network of meteorological observers in the 1780s through the Palatine Meteorological Society in Manheim, followed De Luc closely for the specification of meteorological instruments including thermometers.⁴⁴

3. CALORIC CONSEQUENCES

Attack on the method of mixtures

The consensus about De Luc's thermometry began to crumble just as it was being secured. Trouble developed around the crucial assumption that the amount of heat needed to warm a given amount of water was proportional to the amount of change in its temperature. In presenting the results presented in Table 2 above, De Luc supposed that it would take the same amount of heat to raise the temperature of a given amount of water by five degrees anywhere in the range between 0° and 80°. When applied generally, this came down to the assumption that the specific heat of water did not depend on temperature. De Luc had no reason to doubt it when he wrote *Recherches*. The growing sophistication of the caloric theories, which is the main feature in the development of the chemistry and physics of heat in the decades around 1800, questioned this comfortable uniformity.

All caloric theories shared the basic assumption that heat was an all-pervasive fluid, elastic, subtle, and, weightless, or nearly so. The theories differed on important matters, however, like the behavior of specific heats with temperature. According to Irvine, the amount of caloric contained in a body was the product of its capacity for caloric and its absolute temperature (which would be zero degrees at the point of a total deprivation of heat). In his view, latent heat phenomena resulted from changes in bodies' capacities for caloric: Change of state from ice to water resulted in an increase in the capacity for heat, which meant that more heat was needed to keep the body at the same temperature. The effect was illustrated by analogy to a bucket that suddenly widens; the level of water contained in it would go down, and more water would have to be put in to sustain the level. Irvine explained the heat of chemical reactions similarly, as a consequence of presumed differences between the heat capacities of the reactants and the products.

Although the assumption of constant specific heat for a given state of a substance might seem a natural assumption for an Irvinist (and prominent Irvinists such as Crawford and Thomson did indeed endorse De Luc's method of mixtures),

43. Ernst Gottfried Fischer, *Physique mécanique*, 2nd edn., trans. J.-B. Biot (Paris, 1813), 87, 92, and *Lehrbuch der mechanischen Naturlehre*, 3rd edn., 2 vols. (Berlin, 1827), I, 165.

44. Theodore S. Feldman, "Late enlightenment meteorology," in Tore Frängsmyr, J.L. Heilbron, and Robin E. Rider, eds., *The quantifying spirit in the 18th century* (Berkeley, 1990), 143-177, on 168-169.

John Dalton, a sometime Irvinist, rejected the method altogether. Dalton confessed that he had been “overawed by the authority of Crawford” initially to trust the mercury thermometer, only to be dissuaded by further considerations. Referring to De Luc’s work specifically, Dalton laid the constancy of specific heat open to doubt: “Till this point is settled, it is of little use to mix water of 32° and 212° [Fahrenheit], with a view to obtain the true mean temperature.”⁴⁵ According to Dalton, the mixing of hot and cold water resulted in a slight decrease in volume, hence less space for caloric to fit in, therefore a decrease in heat capacity. That meant, by basic Irvinist reasoning, that temperature would go up. So Dalton thought that mixtures generally had higher temperatures than those given by De Luc’s simple calculations.⁴⁶ Although Dalton may not have had any significant following in thermometry, his argument against De Luc would not have been easy to ignore, since it followed the lines of Dalton’s influential explanation of adiabatic heating and cooling by the mechanical compression and decompression of gases.⁴⁷

De Luc’s method of mixtures was more readily questioned by non-Irvinist caloric theorists, like Black and Lavoisier, who inclined toward a chemical view of heat. In his pioneering work on latent heat, Black postulated, for instance, that the caloric apparently spent in melting ice was not destroyed but merely converted into a different state and so made unable to affect the thermometer. Although Black himself remained agnostic about the nature of heat, many chemists understood his concept of latent heat as implying that caloric could enter into chemical combinations with ordinary matter.⁴⁸ Lavoisier developed a similar view through the 1770s and included caloric (and also light) in the table of chemical elements in his authoritative *Traité élémentaire de chimie* (1789).⁴⁹ On this chemical view of heat, the latent caloric that entered into combination with particles of matter caused increased fluidity as solids melted into liquids and liquids evaporated into gases; latent caloric would become sensible again in condensation or congelation. The absorption and emission of heat in ordinary chemical reactions were explained in

45. John Dalton, *A new system of chemical philosophy*, 1, part 1 (Manchester, 1808), 11, 49–50.

46. *Ibid.*, 3–9; Robert Fox, “Dalton’s caloric theory,” in D.S.L. Cardwell, ed., *John Dalton and the progress of science* (Manchester, 1968), 187–202. Dalton advanced a complex theoretical and experimental argument that the expansion of mercury was quadratic rather than linear with temperature and devised a new temperature scale on the basis of this belief. Dalton (ref. 45), 9f, and also D.S.L. Cardwell, *From Watt to Clausius* (Ithaca, 1971), 124–126.

47. John Dalton, “Experiments and observations on the heat and cold produced by the mechanical condensation and rarefaction of air” *JNP*, 3 (1802), 160–166; originally published in Manchester Literary and Philosophical Society, *Memoirs and proceedings*, 5:2 (1802), 515–526.

48. Black, *Lectures* (ref. 19), 1, 30–35.

49. Henry Guerlac, “Chemistry as a branch of physics: Laplace’s collaboration with Lavoisier,” *HSPS*, 7 (1976), 193–276; Lavoisier, *Elements of chemistry*, trans. Robert Kerr (New York, 1965), 175 (text of 1790).

the same manner. The terms "combined" and "free" caloric entered the terminology alongside the more phenomenological "latent" and "sensible" caloric.⁵⁰

Since combined or latent caloric did not register on thermometers, judging their correctness required knowing how much of the caloric added to a body remained free and how much became combined. Unfortunately, the manner of the transition of caloric between its combined and free states remained under serious dispute. This threw the question of specific heat wide open: specific heat measured the *total* heat used in raising the temperature of a body by a unit amount, and that would have to include whatever went into the combined state.

This problem caused Haüy to withdraw his advocacy of De Luc in the second edition of his textbook, published just three years after the first. In the first edition Haüy had expressed caution about the material nature of heat and entertained Irvinism as a viable alternative to the chemical theory.⁵¹ In the new edition Haüy committed to the chemical view. Apparently his conversion owed something to Pierre Prevost's theory of the dynamic equilibrium of radiant heat, first published in Geneva in 1791. Chagrined that he had not been aware of this significant work, Haüy wrote Prevost promising that he would treat it adequately in the second edition of his textbook. In mastering Prevost's theory Haüy consulted Laplace, Berthollet, and Biot.⁵²

In the second edition, Haüy emphasized that the expansion of a body and the raising of its temperature were two distinct effects of the caloric that entered it. He attributed the distinction between these two effects to Laplace. Haüy traced expansion to the part of added caloric that became latent, and the raising of temperature to the part that remained sensible.⁵³ Then the crucial question in thermometry became the relation between those two amounts: "if the amount of dilatation is to give the measure of the increase in tension, the amount of the caloric that works to dilate the body must be proportional to the amount that elevates the temperature."⁵⁴ According to Haüy's new way of thinking, the expansion of water would require more caloric at lower temperatures, since it had to overcome stronger intermolecular attraction owing to condensation. Therefore, Haüy argued, the real temperature of a mixture would always be lower than the value given by De Luc's calculations.

In reaching equilibrium, the hot water in the usual mixing experiment gives some heat to the cold water. One part of the loss (say *CI*) results in a contraction of the hot water while the rest (*C2*) serves to cool it; likewise, one part of the caloric

50. Ibid., 19.

51. Haüy (ref. 33), I, 103, 123, 130.

52. Lacroix (ref. 33), 154-156, 160-162.

53. René-Just Haüy, *Traité élémentaire de physique*, 2nd edn. (2 vols., Paris, 1806), I, 86. Haüy (ibid., I, 82) defined temperature as the "tension" of sensible caloric, a notion advanced by Pictet (ref. 30, 10-11) in conscious analogy to Volta's concept of electric tension.

54. Haüy, ibid., I, 160, and *Traité élémentaire de physique*, 3rd edn. (2 vols., Paris, 1821), I, 167.

absorbed by the cold water ($C3$) expands it, and the rest ($C4$) warms it. To know the resulting temperature of the mixture, the mixer must know the quantities $C2$ and $C4$. Since they are not necessarily equal, the temperature of the mixture is not necessarily the arithmetic average of the starting temperatures. Conserving heat, Haüy supposes that $C1+C2=C3+C4$. Then (because of the condensation effect) he reasons that $C3$ is greater than $C1$, so $C2$ must be greater than $C4$. We have $C1 < C3$, $C2 > C4$. Therefore the contraction of the hot water would cause less caloric to be given out than the amount taken up by the expansion of the cold water by the same amount. Here Haüy takes the volume of the mixture to be the sum of the initial volumes. Apparently also assuming that the specific heat of water is constant if we consider only the part of the caloric used to raise temperature, Haüy concluded that the temperature of a mixture would always be below the value calculated by De Luc.⁵⁵

De Luc himself may have recognized this point of uncertainty before Dalton's and Haüy's criticisms were published. He developed his own theoretical view about "fire," the material cause of heat, and as he proceeded he recognized the complications surrounding the concept of specific heat. In his *Idées sur la météorologie* (1786-87) and an updating of the *Recherches* published in 1803, he presented theoretical views that left room for variations of specific heat as a function of temperature.⁵⁶ Crawford reported De Luc's hesitation:⁵⁷

Mr De Luc has, however, himself observed, in a paper, with which he some time ago favoured me on this subject, that we cannot determine with certainty from those experiments, the relation which the expansion of mercury bears to the increments of heat. For when we infer the agreement between the dilatations of mercury and the increments of heat from such experiments, we take it for granted, that the capacity of water for receiving heat, continues permanent at all temperatures between the freezing and boiling points. This, however, should not be admitted without proof.

Crawford still held to the real correctness of mercury thermometers on the basis of an experiment of his own contriving. He placed two open metal cylinders containing air at the temperatures of boiling water and melting ice into communication at their open faces, and inserted a mercury thermometer at the interface. Crawford

55. Haüy, *Traité*, 2nd edn. (ref. 53), 1, 166-167; Haüy, *Traité*, 3rd edn. (ref. 54), 1, 173-174.

56. Jean-André De Luc, *Idées sur la météorologie* (2 vols., London, 1786), 1, 187-189, 206-207, and *Introduction à la physique terrestre par les fluides expansibles* (2 vols., Paris, 1803), 1, 241-244. Contrary to the position that Haüy would adopt, De Luc maintained that both expansion and increase in temperature derived from sensible fire; he criticized Fourcroy for thinking that expansion was due to latent caloric, in one of the two essays attacking Lavoisierian chemistry that he attached to *Introduction à la physique terrestre*. De Luc considered that heat was just another word for the expansive force of fire; therefore the term "latent heat" was nonsensical or at best confusing, and he proposed using "latent fire" instead.

57. Crawford "animal heat" (ref. 35), 32-33 (text of 1788).

believed that the real temperature of air at that boundary was the arithmetic mean of the two extreme temperatures, and that was what his mercury thermometer indicated. From this result he inferred the correctness of the mercury thermometer, and of the method of mixtures. He thus confirmed his belief that the mercury thermometer was almost exactly accurate and disputed De Luc's result that the mercury temperature was appreciably below the real temperature in the middle of the range between the boiling and freezing points of water.⁵⁸ In any case De Luc's statement and Crawford's reliance on a new test show that two of the most important advocates of the method of mixtures came to doubt its theoretical cogency.

Mirage of linearity

If the caloric theories rendered the method of mixtures groundless, what alternative did they present in making the choice of thermometric fluids? Haüy and Dalton agreed only that De Luc was wrong. Dalton thought that the true temperature of a mixture should be higher, Haüy that it should be lower, than De Luc's value. The disagreement was not resolved or even seriously debated.⁵⁹ Instead, most caloric theorists were seduced by an apparently easier way out. Calorist theory taught that the action of heat was most purely manifested in gases, whose tiny material particles were too far apart to exert any sensible forces on each other; therefore, all significant action in gases would arise from the caloric that fills the space between the material particles. The theorist could avoid dealing with the uncertainties of the inter-particle forces altogether.⁶⁰

Faith in the simplicity of the thermal behavior of gases was strengthened enormously by the observation announced in 1802 by Joseph-Louis Gay-Lussac and independently by Dalton that all gases expanded by an equal fraction of their initial volume when their temperature was increased by the same amount.⁶¹ This result led many calorists to assume that gases expanded uniformly with temperature. L.J. Thenard wrote in his highly regarded textbook of chemistry, which he

58. Crawford, *ibid.*, 34-54; cf. Table 2 above.

59. Haüy's reasoning could even have been construed as a further vindication of the mercury thermometer, since in De Luc's mixing experiments mercury did indicate readings lower than the calculated real temperatures! Haüy must have thought that the errors in De Luc's calculations were small, since he still endorsed De Luc's test for showing that mercury was better than alcohol. Haüy, *Traité*, 2nd edn. (ref. 53), I, 165; Haüy, *Traité*, 3rd edn. (ref. 54), I, 172.

60. Robert Fox, *The caloric theory of gases from Lavoisier to Regnault* (Oxford, 1971), chapt. 3.

61. John Dalton, "On the expansion of gases by heat," *JNP*, 3 (1802), 130-135; originally published in Manchester Literary and Philosophical Society, *Memoirs and proceedings*, 5:2 (1802), 595-602. Joseph-Louis Gay-Lussac, "Premier essai pour déterminer les variations des température qu'éprouvent les gaz en changeant de densité, et considérations sur leur capacité pour calorique," Société d'Arcueil, *Mémoires de physique et de chimie*, 1 (1807), 180-203.

dedicated to Gay-Lussac: “all gases, in contrast [to liquids and solids], expand equally, and their expansion is uniform and equal for each degree— $1/266.67$ of their volume at 0° , under atmospheric pressure.”⁶² There was, however, a logical gap in that reasoning, as Dalton and Gay-Lussac both recognized. Even if we grant that the thermal expansion of gases is determined exclusively by temperature, it does not follow that the volume of a gas should be a linear function of temperature. Not all possible functions of one variable are linear!⁶³ Laplace took up the challenge to deduce linearity.

The revival of interest in gas thermometers occurred during the ascendancy of “Laplacian physics,” the defining factor in French physical science between 1800 and 1815.⁶⁴ With the gradual demise of Irvinism, the theoretical lead in the understanding of gases fell to the Lavoisier-Laplace tradition. Laplace worked in close association with the chemist Claude-Louis Berthollet, also a former collaborator of Lavoisier’s, not only in setting out a new program for the physical sciences but also in fostering the next generation of scientists who would carry out the program. Much work was centered, symbolically and literally, in the village of Arcueil, where Berthollet and Laplace lived as neighbors.⁶⁵ Both Laplace and Berthollet subscribed to a radical Newtonian program of explaining all phenomena by the action of central forces operating between point-like particles. Laplace aspired to bring the rigor and exactitude of gravitational theory to the rest of physics: “we shall be able to raise the physics of terrestrial bodies to the state of perfection to which celestial physics has been brought by the discovery of universal gravitation.”⁶⁶ In the first decade of the 19th century Laplace and his followers won wide acclaim by creating new theories of optical refraction, capillary action, and acoustics based on short-range forces.⁶⁷ Heat theory was an obvious next target.

Laplace’s early attempt at an argument for the air thermometer, included in volume 4 of his classic *Traité de mécanique céleste* (1805), was brief and loose.

62. L.J. Thenard, *Traité de chimie élémentaire, théorique et pratique* (4 vols., Paris, 1813), 1, 37.

63. Dalton (ref. 45), 9: “Since the publication of my experiments on the expansion of elastic fluids by heat and those of Gay Lussac, immediately succeeding them...it has been imagined by some that gases expand equally; but this is not corroborated by experience from other sources.” Rather, he thought that gases expanded “in geometric progression to equal increments of temperature” (ibid., 11). See also Gay-Lussac (ref. 61), 208-209, which included the epigraph to this paper. Haüy, who was aware of this point before being distracted by Laplacian theorizing, reported that Gay-Lussac had found the coefficient of thermal expansion of air to vary as a function of temperature; Haüy, *Traité*, 2nd edn. (ref. 53), 1, 263-264.

64. Robert Fox, “The rise and fall of Laplacian physics,” *HSPS*, 4 (1974), 89-136.

65. Maurice Crosland, *The Society of Arcueil: A view of French science at the time of Napoleon I* (London, 1967).

66. Pierre-Simon Laplace, *Exposition du système du monde* (2 vols., Paris, 1796), 2, 198.

67. C.G. Gillispie, with R. Fox and I. Grattan-Guinness, *Pierre-Simon Laplace 1749-1827: A life in exact science* (Princeton, 1997); J.L. Heilbron, *Weighing imponderables and other quantitative science around 1800*, *HSPS*, 24:1 (1993), suppl., 166-184.

There he labelled as “at least very probable” the opinion that the thermometer indicated accurately “the real degrees of heat.” His entire argument consisted of this: “if we imagine the temperature of the air to increase while its volume remains the same, it is very natural to suppose that its elastic force, which is caused by heat, will increase in the same ratio.” He then imagined a relaxation of the external pressure confining the heated gas until the initial pressure was reached; the volume of the gas would have increased in the same ratio as the pressure had done under constant volume. This last step follows from assuming Mariotte's (Boyle's) law.⁶⁸ This non-argument seems to have convinced many people, including the judicious Haüy.⁶⁹ Calorist plausibility combined with Laplacian authority propelled the air thermometer into the position of the “true thermometer” in the eyes of many active researchers. By the 1820s, Thomas Thomson, now Regius Professor of Chemistry at Glasgow, granted that “it is at present the opinion of chemists, that...the expansion of all gases is equable,” thus reversing his own earlier view that “none of the gaseous bodies expand equably.”⁷⁰ The only thing to be said for the mercury thermometer was that it was convenient, and that its readings agreed closely with those of the air thermometer between the freezing and boiling points of water, as shown most famously by Gay-Lussac.⁷¹

Meanwhile Laplace developed a more detailed and quantitative argument. To make the concept of temperature more precise, Laplace adopted the approach of Pierre Prevost, who had defined temperature through the equilibrium of radiant caloric.⁷² Laplace accordingly defined temperature as the density of the caloric in intermolecular spaces produced by the simultaneous emission and absorption of caloric by the molecules. But why should the caloric contained in molecules be radiated away at all? Laplace found the cause in the repulsive force exerted by the caloric contained in nearby molecules. The model might seem to fit well with the old distinction between free and latent caloric: some of the latent caloric contained in molecules would be disengaged by caloric-caloric repulsion and become free caloric. However, that conflicted with Laviosier's concept of a latent caloric chemically bound to matter, incapable of being disengaged from the molecules except through changes of state, chemical reactions, or some unusual physical agitation.

Laplace took the extraordinary step of putting *free* caloric inside molecules. The particles of free caloric were *bound*, but still exerted repulsive forces on each other; this way, free caloric in one molecule could dislodge free caloric from other molecules. On the other hand, latent caloric, also bound in molecules, did not exert repulsive forces, and could be ignored in Laplace's force-based derivations. Laplace

68. Pierre-Simon Laplace, *Traité de mécanique céleste*, 4 (Paris, 1805), xxii.

69. Haüy, *Traité*, 2nd edn. (ref. 53), 1, 167-168; Haüy, *Traité*, 3rd edn. (ref. 54), 1, 174-175.

70. Thomson (ref. 19), 9-10, and (ref. 34), 273, resp. In the first of these texts, Thomson said “it is scarcely possible to demonstrate the truth of this opinion experimentally, because we have no means of measuring temperature, except by expansion,” and added that “the opinion is founded on very plausible reasons,” without giving the reasons.

71. Laplace (ref. 68), xxi-xxii, 270; Gay-Lussac (ref. 61).

72. Pierre Prevost, “Sur l'équilibre du feu,” *Journal de physique*, 38 (1791), 314-323.

called free caloric disengaged from molecules *free caloric of space*, which was a third state of caloric (very similar to the older notion of radiant caloric), in addition to Lavoisier's latent/combined caloric and free/sensible caloric.⁷³

Laplace supposed that there would be a correlation between the density of free caloric contained in molecules and the density of free caloric tossing about in intermolecular spaces because the amount of caloric being removed from a given molecule would clearly be a function of the intensity of the cause of the removal. So the density of free caloric of space could be used for the measurement, even definition, of temperature. With this model of temperature, Laplace's argument that the air thermometer was "the true thermometer of nature" consisted in showing that the volume of air under constant pressure would be proportional to the density of the free caloric of space.⁷⁴

An intuitive, or, better, semi-quantitative deduction of this proportionality may be paraphrased as follows.⁷⁵ Laplace took as his basic relations

$$P = K_1 \rho^2 c^2, \quad T = K_2 \rho c^2,$$

where P is the pressure, T the temperature, K_1 and K_2 constants, ρ the density of the gas, and c the amount of free caloric contained in each molecule. The first relation follows from regarding the pressure of a gas as resulting from the repulsion of caloric contained in it. The repulsion between any two molecules would be proportional c^2 ; the pressure exerted by a molecular layer of density ρ on a surface layer of the same density is proportional to ρ^2 . In favor of the second relation Laplace argued that temperature, the density of free caloric in the intermolecular space, would be proportional to the quantity of caloric emitted (and absorbed) by each molecule in unit time. This quantity would be proportional to the density of caloric present in its environment, ρc , and also to the amount of free caloric in the molecule available for removal, that is, c . By combining the relations, Laplace had $\rho = \text{const. } T/V$, where V is the volume occupied by the given amount of gas that is, the laws of Charles and Guy-Lussac. For fixed P , T is proportional to V : the volume of a gas under constant pressure gives a true measure of temperature.

It remained to make the quantitative argument by writing down the force between two caloric particles as a function of distance and performing the appropriate integrations to calculate the aggregate effects. Unfortunately, Laplace had no

73. Pierre Simon Laplace, "Sur l'attraction des corps spheriques et sur la répulsion des fluides élastiques," *MAS*, 5 (1821-22), 1-9, on 7; Laplace, *Traité de mécanique céleste*, 5 (Paris, 1825), 93, 113; Laplace, "Sur l'attraction des sphères, et sur la répulsion des fluides élastiques," *Connaissance des Temps*, pour l'an 1824 (1821), 328-343, on 335.

74. Laplace, "corps" (ibid.), 4: The "extreme rarity," of the intermolecular caloric (owing to its high speed of transmission), guaranteed that the amount of free caloric of space in a body would be a negligible fraction of the total amount of free caloric contained in it; the former could serve as a measure of the latter, without actually constituting a significant portion of it.

75. This follows the exposition in ibid., 3-6, supplemented by insights taken from Laplace, *mécanique* (ref. 73), book 12. See also S.G. Brush, *Kinetic theory*, Vol. 1 (Oxford, 1965), 12-13.

idea what the inter-caloric force function looked like. In his derivations Laplace wrote $f(r)$ for the unknown aspect of that function and introduced symbols for its various integrals. He gave the unknown expression in the final formula, a definite integral, the symbol K and treated it as a constant for a given type of gas; it turned out not to matter for anything important. The real work in the derivation was done by other assumptions made along the way.⁷⁶ These assumptions make an impressive list. In addition to the basic calorist picture of a gas, Laplace assumed that the gas would be in thermal equilibrium and uniform in density; that its molecules would be spherical, stationary, and very far apart from one another; that each molecule would contain exactly the same amount of caloric; that the force between the caloric particles would be a function of distance and nothing else, and negligible at any sensible distances; that the particles of the free caloric of space moved at a remarkably high speed; and so on.⁷⁷

Since these assumptions were not theoretically defended or empirically testable, even most French theorists did not follow up Laplace's calculations on caloric. The sole exception worth noting is Siméon-Denis Poisson, who, according to Fox, "seems to have pursued the [Laplacian] program with even greater zeal than the master himself."⁷⁸ But few people bothered to argue about the details of Laplace's caloric theory. Rather, its rejection was made wholesale amid the general decline and rejection of the Laplacian research program.⁷⁹ However discredited, Laplace's treatment of gases was the only viable theoretical account until the revival and further development of Sadi Carnot's work in the 1840s and 1850s, and the only viable microphysical account until the advent of the kinetic theory in the latter half of the century.

4. EMPIRIC THERMOMETRY

The dominant climate in French physics after Laplace was empiricist, with two major preoccupations: phenomenological analysis in theory, and precision in experiment. In thermal physics the phenomenalist trend seems to have been a direct reaction against Laplacianism; at any rate it constituted a loss of nerve in theorizing about unobservable entities. The rise of Jean Baptiste Joseph Fourier

76. A similar view is given by Heilbron (ref. 67), 178-180, and Clifford Truesdell, *The tragicomical history of thermodynamics, 1822-1854* (New York, 1979), 32-33. Laplace had made similar calculations for capillary action and optical refraction; see Fox (ref. 64), 101, and Heilbron (ref. 67), 171-178.

77. Laplace, "sphères" (ref. 73), 332-335.

78. Fox (ref. 64), 120-121, 127 (quote); Siméon-Denis Poisson, *Théorie mathématique de la chaleur* (Paris, 1835).

79. One of the exceptions here was the Scottish mining engineer Henry Meikle, who attacked Laplace's treatment of thermometry directly with a cogent technical argument. See Henry Meikle, "Thermometer," *Encyclopaedia britannica*, 7th edn. (1842), 21, 236-242; Henry Meikle, "On the theory of the air-thermometer," *Edinburgh new philosophical journal*, 1 (1826), 332-341.

was symptomatic. Although one of Napoleon's favorite savants, Fourier was an outsider in the scientific circles at the height of Laplace's dominance. He started his work on heat theory around 1805 while in Grenoble, serving as the prefect of the department of Isère after accompanying Napoleon on his Egyptian expedition. His work on heat conduction, despite not being based on the caloric theory at all, won the 1811 prize competition of the French Institute. However, it was denied publication in the *Mémoires* of the Institute, and saw the first light of day only in 1822 as a monograph entitled *Théorie analytique de la chaleur*. By then Laplace's age was almost over. That same year, 1822, Fourier was elected permanent secretary for the mathematical sciences of the Paris Academy. His work now stimulated great interest in both thermal physics and mathematics. Fourier became, in Fox's estimation, "a benign, influential, but rather detached patron of the new generation," the anti-Laplacian rebels including Pierre Dulong, Alexis-Thérèse Petit, François Arago, and Augustin Fresnel as the most important figures.⁸⁰

In his theorizing Fourier eschewed all consideration of deep causes. His starting point was simply that there be some initial distribution of heat, and some specified temperatures on the boundaries of the body being considered; he did not concern himself with the mechanisms that produced and maintained these initial and boundary conditions. Then he produced equations that would predict the observed change in the initial distribution over time. This aspect of Fourier's work had a strong affinity to positivist philosophy. Fourier attended the lectures of Auguste Comte on positivism in 1829; Comte for his part admired Fourier's work, so much so as to dedicate his *Cours de philosophie positive* to Fourier (and to Henri Marie Ducrotay de Blainville, the anatomist and zoologist).⁸¹

Contrary to the Laplacian dream of the one Newtonian method applied to all of the universe, the special power and attraction of Fourier's work lay in a conscious and explicit narrowing of focus. The theory of heat proper would only deal with what is *not* reducible to the laws of mechanics: "whatever may be the range of mechanical theories, they do not apply to the effects of heat. These make up a special order of phenomena, which cannot be explained by the principles of motion and equilibrium." Fourier was happy to leave interparticulate and caloric forces to Laplace and his school for their corpuscularian analysis.⁸² Truly thermal phenomena were *movements* of heat through undisturbed material structures. Fourier's theory of heat left out most of the traditional concerns of heat theory.⁸³ The expan-

80. Fox (ref. 64), 110, 120 (quote).

81. Fox (ref. 60), 265-266. Cf. Ernst Mach, *Principles of the theory of heat (historically and critically elucidated)*, trans. T.J. McCormack, P.E.B. Jourdain and A.E. Heath, ed. Brian McGuinness (Dordrecht, 1986), 113: "Fourier's theory of the conduction of heat may be characterized as an ideal physical theory....The entire theory of Fourier really consists only in a consistent, quantitatively exact, abstract conception of the facts of conduction of heat—in an easily surveyed and systematically arranged *inventory* of facts."

82. Joseph Fourier, *The analytic theory of heat*, trans. Alexander Freeman (New York, 1955), 2, 11-12, 23; originally published as *Théorie analytique de la chaleur* (Paris, 1822).

83. It is not clear whether Fourier thought that the flow of heat was not reducible to me-

sive effects of heat also fell outside Fourier's domain. Therefore there was no possibility that the tradition of heat theory established by Fourier could help elucidate the workings of the thermometer. That did not seem to bother Fourier.⁸⁴

The phenomenalist trend away from microphysics was broader than Fourier's study of heat conduction. Another important approach occurred in the work of Sadi Carnot. Like the early Fourier, Carnot worked on the fringes of the Laplace-dominated Paris scientific community, but unlike Fourier he did not live to see the eventual acceptance of his neglected work. Carnot's now famous *Réflexions* of 1824 was based on a provisional acceptance of the caloric theory, but it steered away from microphysical reasoning. His analysis of the ideal heat engine sought relations between the macroscopic parameters pertaining to a body of gas: temperature, pressure, volume, and quantity of heat. All but the last of these variables were directly measurable. Emile Clapeyron's revival of Carnot's work in 1834 continued in this macroscopic-phenomenological vein. The Carnot-Clapeyron theory only made use of the presumably known relations regarding thermal expansion, and could not make any contributions toward their theoretical justification.⁸⁵

Experimental precision was the other major preoccupation in the empiricism that came to dominate 19th-century French physics. According to many historians, the quest for precision originated in the "quantifying spirit" of the Enlightenment,⁸⁶ which continued to develop through and beyond the heyday of Laplace. Berthollet and Laplace actively encouraged the development of precision experiment in the work of their protégés. The Arcueil circle started to achieve the precision claimed by Lavoisier.⁸⁷ The bright light in the early phase was Gay-Lussac, on whom Laplace and Berthollet routinely depended for precision experiments in both physics and chemistry.⁸⁸ The most memorable of these was his work on the expansion of gases. Other contributors to precision experiment included Jean-Joseph Welter, François Delaroche and Jacques Étienne Bérard, all of whom worked to improve measurements of the specific heats of gases.

chanical actions between caloric particles; he certainly did not consider such a reduction plausible in 1822.

84. *Ibid.*, 26-27.

85. Nicolas-Léonard-Sadi Carnot, *Reflections on the motive power of fire*, trans. and ed. Robert Fox (Manchester, 1986), originally published as *Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance* (Paris, 1824); Benoit-Pierre-Émile Clapeyron, "Memoir on the motive power of heat," trans. Richard Taylor, *Scientific memoirs, Selected from the transactions of foreign academies of science and learned societies and from foreign journals*, 1 (1837), 347-376; originally published as "Mémoire sur la puissance motrice de la chaleur," *Journal de l'école polytechnique*, 14 (1834), 153-190.

86. Frängsmyr et al. (ref. 44); M. Norton Wise, ed., *The values of precision* (Princeton, 1995).

87. Jan Golinski, "'The nicety of experiment': Precision measurement and precision of reasoning in late eighteenth-century chemistry," in Wise (*ibid.*), 72-91, esp. 78.

88. Crosland, *Society of Arcueil* (ref. 65), and Gay-Lussac: *Scientist and bourgeois* (Cambridge, 1978).

The highest acclaim for precision in this period, however, went to Pierre-Louis Dulong and Alexis-Thérèse Petit, both identified by Fox as leading rebels against Laplacian physics. Since Petit died at the age of 28 not having fulfilled his spectacular promise, he is mostly remembered by the three joint papers he published with Dulong. Dulong's complex career can be divided into three phases: the chemist most famous for his intrepid experiments with the highly explosive nitrogen trichloride, his own creation; Petit's collaborator in precision measurements in thermal physics; after Petit's death, the head of the government-sponsored committee to study the operation of steam boilers.⁸⁹ The Dulong-Petit collaboration is best known now for their controversial "law of atomic heat" announced in 1819 (that the product of atomic weight and specific heat is constant for all elements); however, and significantly for our story, it was their two previous joint papers on thermal expansion, the laws of cooling and thermometry (1816 and 1817), that won them the respect of their peers at home and abroad.

In retrospect, Dulong and Petit's decisive contribution to thermometry was to highlight the urgency of making a rational choice of thermometric fluid. This they achieved in two ways. For one, they demonstrated the magnitude of the mercury-air discrepancy. While confirming Gay-Lussac's earlier result that the mercury thermometer and the air thermometer agreed perfectly well between the freezing and boiling points of water, Dulong and Petit carried the comparison to high temperatures, where no one before them had been able to make accurate determinations. They showed that the discrepancy increased as temperatures went up, reaching around 10 degrees at around 350 degrees centigrade (mercury giving higher numbers).⁹⁰ Evidently, the two thermometric fluids could not be used interchangeably. The second achievement was experimental. The extraordinary care and virtuosity of their measurements made it implausible to attribute the discrepancy to experimental error. They were justly proud of this achievement and asserted that they had reached the highest possible precision in this type of experiment.⁹¹ No one credibly challenged their confidence—until Regnault.

Dulong and Petit had a straightforward requirement for a true thermometer. If additions of equal amounts of heat produce equal increases in the volume of a substance, then that is the perfect thermometric substance.⁹² However, they did not think that this condition was amenable to a direct empirical test, since the

89. For a detailed discussion of Dulong and Petit's work, see Fox (ref. 60), 227-270. Pierre Lemay and Ralph E. Oesper, "Pierre Louis Dulong, his life and work," *Chymia*, 1 (1948), 171-190.

90. Pierre-Louis Dulong and Alexis-Thérèse Petit, "Recherches sur la mesure des températures et sur les lois de la communication de la chaleur," *Annales de chimie et de physique*, 7 (1817), 113-154, on 117-120, including a summary of results in Table 1 on 120. See also Pierre-Louis Dulong and Alexis-Thérèse Petit, "Recherches sur les lois de dilatation des solides, des liquides et des fluides élastiques, et sur la mesure exacte des températures," *Annales de chimie et de physique*, 2 (1816), 240-263, on 250 and 252.

91. Dulong and Petit, "la mesure" (ibid.), 119, and "les lois" (ibid.), 245-249.

92. Dulong and Petit, "la mesure" (ref. 90), 116.

quantity of heat could not be measured with sufficient exactness, especially at higher temperatures. Instead they outlined the following strategy: start by observing, using the standard mercury thermometer, the thermal expansion of some candidate substances among the gases and metals.⁹³ What they expected from these observations seems to be something like the following. If many substances display the same pattern of thermal expansion, then each of them should be taken to be expanding uniformly. This agreement would indicate that disturbing factors are not significant because the disturbing factors, different for different substances, would not be likely to result in exactly the same distortions in the pattern of expansion. Their empirical research revealed that metals did not fulfill this expectation of uniformity. They concluded that gases were the best thermometric substances.⁹⁴

The argument does not constitute any theoretical advance over the earlier calorist inference that Gay-Lussac and Dalton had enough perspicuity to distrust. As Dulong and Petit themselves recognized, theirs was only a plausibility argument, and the plausibility was significantly diminished in the absence of the support by the calorist metaphysics of mutually attracting matter particles held apart by the self-repulsive caloric. The experimental basis of this view also showed little progress, since Dulong and Petit do not seem to have carried out any extensive new work showing the uniformity of thermal expansion in different types of gases. Their papers reported only experiments on atmospheric air.⁹⁵

5. A PROVISIONAL END

Austerity

The principles of thermometry thus endured "the rise and fall of Laplacian physics" and returned to almost exactly where they began. The two decades following Dulong and Petit's work discussed above were characterized by a continuing erosion of confidence in all theories of heat. The consequence was a widespread skepticism and agnosticism about all doctrines going beyond observations. This loss of confidence resulted in a loss of theoretical interest and sophistication.⁹⁶ An emblematic figure for this period is Gabriel Lamé, renowned mathematician, physicist, and engineer. A disciple of Fourier's, Lamé also modelled himself after Dulong and Petit. Here is his position:

MM. Petit and Dulong constantly sought to free teaching from those doubtful and metaphysical theories, those vague and thenceforth sterile hypotheses which used to make up almost the whole of science before the art of experimenting was perfected to the point where it could serve as a reliable guide....[After their work] it could be imagined that at some time in the future it would be possible to make the

93. Dulong and Petit, "les lois" (ref. 90), 243.

94. Dulong and Petit, "la mesure" (ref. 90), 136-150, 153.

95. Dulong and Petit, "les lois" (ref. 90), 243.

96. Fox (ref. 60), 261-262, 276-279.

teaching of physics consist simply of the exposition of the experiments and observations which lead to the laws governing natural phenomena, without it being necessary to state any hypothesis concerning the first cause of these phenomena that would be premature and often harmful. It is important that science should be brought to this positive and rational state.

This attitude won Lamé the admiration of Comte, who had been his classmate at the *École polytechnique*.⁹⁷

Lamé discussed the choice of thermometric fluids in his textbook of physics for the *École*. He agreed that gases seemed to reveal, better than other substances, the pure action of heat unadulterated by the effects of intermolecular forces. However, like Dalton and Gay-Lussac (and Haüy before his Laplacian indoctrination), Lamé recognized the limits to the conclusions derivable from that assumption.⁹⁸

Although the indications of the air thermometer could be regarded as exclusively due to the action of heat, from that it does not necessarily follow that their numerical values measure the energy of that action in an absolute manner. That would be to suppose without demonstrating it that the quantity of heat possessed by a gas under a constant pressure increases proportionally to the variation of its volume. If there were an instrument for which such a proportionality actually held, its indications would furnish an absolute measure of temperatures; however, as long as it is not proven that the air thermometer has that property, one must regard its reading as an as yet unknown function of the natural temperature.

Into this state of resignation entered Henri Victor Regnault, with a solution forged in a most austere version of post-Laplacian empiricism. In his prime Regnault was regarded as the best experimental physicist in all of Europe. Paul Langevin, though critical of him, drew a parallel between Regnault's rise and the glory days of Napoleon.⁹⁹ Orphaned at the age of two, Regnault benefited from the meritocratic educational system created by the French Revolution. With ability and determination alone he gained his entry to the *École polytechnique*, and by 1840, at the age of 30, succeeded Gay-Lussac as Professor of Chemistry there. In that same year he was elected to the chemistry section of the *Académie des sciences* and in the following year became Professor of Experimental Physics at the *Collège de France*. By then he was the obvious choice for the renewed commission from the Minister of Public Works to determine all the data and empirical laws relevant to the study and operation of steam engines.

Thus ensconced in a prestigious institution with ample funds and few other duties, Regnault not only supplied the government with the needed information,

97. Gabriel Lamé, *Cours de physique de l'École Polytechnique* (Paris, 1836), I, ii-iii. The translation is from Fox (ref. 60), 269-270.

98. Lamé (*ibid.*), I, 256-258.

99. Paul Langevin, "Centenaire de M. Victor Regnault," *Collège de France, Annuaire*, 11 (1911), 42-56, on 44.

but in the course of the work also established himself as an undisputed master of precision measurement. Marcelin Berthelot later recalled the strong impression he had received on meeting Regnault in 1849: “It seemed that the very genius of precision had been incarnated in his person.”¹⁰⁰ Young scientists from all over Europe, ranging from William Thomson (later Lord Kelvin) to Dmitri Mendeleev, visited his laboratory, and many stayed to work and learn as his assistants.¹⁰¹ Pierre Duhem credited Regnault with having effected “a true revolution” of precision in experimental physics.¹⁰² Others have agreed that Regnault’s influence was long-lasting. “Regnault founded a school with his method—every physicist today conforms to it.” “For at least twenty-five years, the methods and the authority of Regnault dominated all of physics and became imperative in all research and teaching. Scruples for previously unknown degrees of precision became the dominant preoccupation of the young school.”¹⁰³

Regnault may have frightened the European scientific community into accepting the authority of his results. The size of Regnault’s equipment alone might have been enough to overpower potential detractors! Regnault describes in one place a manometer 24 meters tall that he constructed for the measurement of pressure up to 30 atmospheres, later a famous attraction in the old tour of the Collège.¹⁰⁴ Dörries states that it was difficult for other physicists to challenge Regnault’s results because they could not afford the equipment needed to repeat his experiments. The sheer volume and thoroughness of his output would have had the same effect. Regnault’s reports relating to the steam engine took up three entire volumes of the *Mémoires* of the Paris Academy, each one numbering 700 to 900 pages, bursting with tables of precise data and interminable descriptions of experimental procedures. In describing the first of these volumes, James David Forbes spoke of “an amount of minute and assiduous labor almost fearful to contemplate.”¹⁰⁵

What set Regnault apart was not mere diligence and affluence. Dumas observed that Regnault introduced a significant new *principle* to experimental phys-

100. Ibid.

101. A list of these visitors is given by Jean-Baptiste Dumas, “Victor Regnault” [1881], in J.-B. Dumas, *Discours et éloges académiques* (2 vols., Paris, 1885), 2, 153–200, on 178. Crosbie Smith and M. Norton Wise, *Energy and empire: A biographical study of Lord Kelvin* (Cambridge, 1989), 104–108; Bernard Jaffe, *Crucibles: The story of chemistry from ancient alchemy to nuclear fission*, 4th edn. (New York, 1976), 153 (on Mendeleev).

102. Pierre Duhem, “Usines et laboratoires,” *Revue philomathique de Bordeaux et du Sud-Ouest*, 2 (1899), 385–400, on 392.

103. Resp. Dumas (ref. 101), 174, and Edmond Bouty, “La physique,” in *La science française* (2 vols., Paris, 1915), 1, 131–151, on 139.

104. Victor Regnault, “Relations des expériences entreprises par ordre de Monsieur le Ministre des Travaux Publics, et sur la proposition de la Commission Centrale des Machines à Vapeur, pour déterminer les principales lois et les données numériques qui entrent dans le calcul des machines à vapeur,” *MAS*, 21 (1847), 1–748, on 349; Langevin (ref. 99), 53.

105. Matthias Dörries, “Easy transit: Crossing boundaries between physics and chemistry in mid-nineteenth century France,” in Jon Agar and Crosbie Smith, eds., *Making space for science: Territorial themes in the shaping of knowledge* (Basingstoke, 1998), 246–262, on 258;

ics, which he regarded as a service to science that would never be forgotten. Dumas contrasted Regnault's methodology with that exhibited in the classic treatise of physics by Jean-Baptiste Biot. Where Biot used simple apparatus to make observations and then reasoned clearly through all the necessary corrections, Regnault realized (as Dumas put it): "In the art of experimenting by way of corrections, the only sure procedure is that which does not require any." Dumas summed up Regnault's distinctive style of as follows:¹⁰⁶

A severe critic, he allows no causes of error to escape him; an ingenious spirit, he discovers the art of avoiding all of them; an upright scholar, he publishes all the elements relevant to the discussion, rather than merely giving mean values of his results. For each question he introduces some characteristic method; he multiplies and varies the tests until no doubts remain about the character of the results.

Regnault had come to physics from chemistry through the study of specific heats in relation to Dulong and Petit's law.¹⁰⁷ After finding the law to be only approximate, as many others had suspected, he turned to the more trusted regularities regarding the behavior of gases. As Regnault increased the precision of his tests, he was able to refute two laws that had been regarded as fundamental truths: that all gases expand to the same extent between the same limits of temperature (the law of Gay-Lussac and Dalton), and that a given gas expands to the same extent between the same limits of temperature regardless of its initial density (the law of Amontons).¹⁰⁸ In his memoir of 1847, Regnault repeated these results with further details and also showed that Mariotte's (or Boyle's) law was only approximately and erratically true.¹⁰⁹

James David Forbes, "Dissertation sixth: Exhibiting a general view of the progress of mathematical and physical science, principally from 1775 to 1850," *Encyclopaedia britannica*, 8th edn., 1 (1860), 794-996, on 958.

106. Dumas (ref. 101), 169, 174. For example, if one puts a sizable glass vessel containing a gas on one side of the balance and small metal weights on the other, the apparent measured weight of the gas must be corrected by estimating the effect of the buoyancy of the surrounding air, for which it is necessary to know the exact pressure and temperature of the air, the exact density and volume of the glass, etc. Regnault eliminated the need for the correction by hanging an identical glass vessel, only evacuated, on the other side of the balance, which then behaved as if it were in a perfect vacuum.

107. *Ibid.*, 162; Victor Regnault, "Recherches sur la chaleur spécifique des corps simples et composés," *Annales de chimie et de physique*, 73 (1840), 5-72.

108. Victor Regnault, "Recherches sur la dilatation des gaz," *Annales de chimie et de physique*, 4 (1842), 5-67 (first memoir), 52-83 (second memoir).

109. Regnault (ref. 104), esp. 91, 119-120, 148-150, 367-401. Regnault showed that Mariotte's law held for carbonic acid at 100°C but not at 0°C, even at low densities; seldom for atmospheric air and nitrogen; occasionally for hydrogen which, however, departed from the law in the opposite direction to air and nitrogen.

After these experiences he eschewed reliance on accepted laws and did not take much interest in the new theoretical speculations issuing from the fickle minds of Faraday, Ørsted, Joule, and Mayer, whom posterity has praised for their bold ideas.¹¹⁰ When De Luc said, "The moral and physical microscope are equally fit to render men cautious in their theories," he could not have anticipated the spirit of Regnault's work any better.¹¹¹ In Marcellin Berthelot's estimation, Regnault was "devoted to the search for pure truth, but that search he envisioned as consisting above all in the measurement of numerical constants. He was hostile to all theories, keen to emphasize their weaknesses and contradictions." For Regnault, to search for truth meant: "to replace the axioms of theoreticians by precise data."¹¹²

Regnault hoped to be able to test *all* assumptions by measurements. "In establishing the fundamental data of physics one must, as far as possible, only make use of direct methods."¹¹³ Regnault aimed at a puritanical removal of theoretical assumptions in the design of all basic measurement methods. This was, however, easier said than done. How can any measurement instruments be designed, if one can make no assumptions about how the material substances that constitute them behave? Each experiment had to take something for granted. Regnault's conscience then forced him to engage in further experiments to test these somethings. The process had no end. Regnault got caught up in what Dörries has characterized as a never-ending circle of "experimental virtuosity." Regnault's original intention had been to start with observations cleansed of theory, then to move on to careful theorizing on the basis of the indisputable data. But the task of obtaining indisputable data turned out to be unending.¹¹⁴

Later appraisals of Regnault, both by scientists and by historians, have tended to be more reserved than the praise of his contemporaries. Fox acknowledges Regnault's "monumental achievements" but judges his "preoccupation with the tedious accumulation of results" as unfortunate, especially in view of "the momentous developments in physics taking place outside France during the 1840s." Regnault himself seems to have been exasperated with the impossibility of moving on beyond metrological worries.¹¹⁵ However, the advances that Regnault made were genuine and lasting, not least in thermometry. He found the best solution in the long search for the "real" scale of temperature.

110. Dumas (ref. 101), 191.

111. De Luc, *Essay on pyrometry and areometry, and on physical measurements in general* (London, 1779), 20.

112. Quoted in Langevin (ref. 99), 44-45, and Dumas (ref. 101), 194, resp.

113. Quoted in Langevin (ref. 99), 49.

114. Matthias Dörries, "Vicious circles, or, The pitfalls of experimental virtuosity," in Michael Heidelberger and Friedrich Steinle, eds., *Experimental essays—Versuche zum Experiment* (Baden-Baden, 1998), 123-140, esp. 128-131.

115. Matthias Dörries, *Visions of the future of science in nineteenth-century France (1830-1871)* (Habilitation thesis, Munich, 1997), 162-164. Fox (ref. 60), 295, 299-300.

Comparability

The secret of Regnault's success in thermometry was the idea of "comparability." If a type of thermometer is to be an accurate instrument, all thermometers of that type must agree with each other in their readings. Regnault considered this "an essential condition that all measuring apparatuses must satisfy."¹¹⁶ Comparability suited his mistrustful metrology. All that he assumed was that a real physical quantity should have one unique value in a given situation.

The requirement of comparability was not new with Regnault. It had been widely considered a basic requirement for reliability in thermometry for a long time. The term is more easily understood if we go back to its origin, namely when thermometers were notoriously unstandardized so the readings of different types of thermometers could not be meaningfully *compared* with one another. Regnault transformed this old notion of comparability into a powerful tool for testing the goodness of each given type of thermometer. The novelty he introduced was a higher degree of skepticism. Standard methods of calibration only involved making different thermometers with each other at a small number of points. Regnault recognized that agreement at other points was a hypothesis open to empirical tests.

De Luc grew accustomed to thinking about comparability through his famous work in barometry.¹¹⁷ In thermometry he used the comparability criterion to give an additional argument against the spirit thermometer. De Luc's results, some of which are summarized in Table 4, showed that spirit expanded according to different laws depending on its concentration.¹¹⁸ But why was it not possible to avoid this difficulty by specifying a standard concentration of the spirit to be used in thermometers? That would have created another fundamental difficulty, of having to measure the concentration accurately. This was not easy, as we can see in the extended essay on areometry (the measurement of the specific gravity of liquids) that De Luc published seven years later.¹¹⁹

Since the spirit thermometer had been discredited beyond rescue in terms of comparability (and in other ways), Regnault's main concern was to evaluate the air thermometer and the mercury thermometer. With regard to comparability, mercury betrayed clearer signs of trouble. Regnault found that there was no such thing as "the" mercury thermometer. Mercury thermometers made with different types of glass differed from each other even if calibrated to read the same at the fixed points. The divergence was noticeable particularly at temperatures above 100° centigrade, as shown in Table 5.

116. Regnault, "Relations des expériences" (ref. 104), 164.

117. De Luc (ref. 12), *I*, part 2, chapt. 1, and De Luc (ref. 111), 93f.

118. De Luc (ref. 12), *I*, 326. De Luc assumed that mercury thermometers were inter-comparable. Since mercury is a homogeneous liquid and does not mix well with anything else, De Luc thought that its concentration was not likely to vary. Haüy, *Traité* (ref. 33), 142-143 (and corresponding passages in subsequent editions), and Lamé (ref. 97), 219, accepted the comparability of the mercury thermometer.

119. De Luc (ref. 12), *I*, 327-328, and De Luc (ref. 111).

Table 4. De Luc's comparison of spirit thermometers made with different concentrations of spirit^a

<i>mercury</i>	highly distilled spirit ^b	Réaumur's spirit ^c	brandy	1 part spirit, 1 part water	old Languedoc wine	1 part spirit, 3 parts water	<i>water</i>
80	80.0	80.0	80.0	80.0	80.0	80.0	80.0
75	73.8	73.9	73.4	73.2	72.4	71.6	71.0
70	67.6	67.8	67.4	66.7	64.3	62.9	62.0
65	61.5	61.8	61.4	60.6	56.6	55.2	53.5
60	55.5	56.2	55.6	54.8	49.5	47.7	45.8
55	50.3	50.5	49.8	49.1	42.5	40.6	38.5
50	45.1	45.0	44.4	43.6	36.2	34.4	32.0
45	40.0	39.8	39.2	38.4	30.1	28.4	26.1
40	35.0	35.0	34.2	33.3	24.6	23.0	20.5
35	30.1	30.1	29.4	28.4	19.9	18.0	15.9
30	25.5	25.5	24.7	23.9	15.3	13.5	11.2
25	20.9	20.8	20.3	19.4	11.2	9.4	7.3
20	16.5	16.3	15.9	15.3	7.7	6.1	4.1
15	12.0	11.9	11.8	11.1	4.9	3.4	1.6
10	7.9	7.9	7.7	7.1	2.3	1.4	0.2
5	3.9	3.9	3.8	3.4	0.9	0.1	-0.4
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

a. De Luc (ref. 12), I, 326.

b. This is specified as obtainable by distilling spirit already strong enough to ignite gunpowder further in a sand bath.

c. This is the concentration that Réaumur had used in his spirit thermometers, 5 parts concentrated spirit and 1 part water.

Table 5. Regnault's comparison of mercury thermometers made with different types of glass^a

ordinary glass	crystal	difference
0 °C	0 °C	0 °C
100	100	0
190.51	191.66	1.15
246.68	249.36	2.68
251.87	254.57	2.70
279.08	282.50	3.42
310.69	315.28	4.59
333.72	340.07	6.35

a. Victor Regnault, "Sur la comparaison du thermomètre à air avec le thermomètre à mercure," *Annales de chimie et de physique*, 5 (1842), 83-104, on 100-103; the table is adapted from that on 102.

Worse yet, examples of the same type of glass that had undergone different thermal treatments did not follow the same law of expansion. Regnault laid to waste the assumed comparability of the mercury thermometer in his painstaking series of experiments on eleven different instruments made with four different types of glass (see Table 6, containing results showing differences over 5° in some cases). It was as if Fahrenheit's ghost had revisited the scene with a grin.

Table 6. Regnault's comparison of mercury thermometers made with different types of glass^a

air thermometer	mercury with "Choisy-le- Roi" crystal	mercury with ordinary glass, thermo- meter no. 5	mercury with green glass, thermometer no. 10	mercury with Swedish glass, thermo- meter no. 11
100 °C	100.00	100.00	100.00	100.00
150	150.40	149.80	150.30	150.15
200	201.25	199.70	200.80	200.50
250	253.00	250.05	251.85	251.44
300	305.72	301.08	-	-
350	360.50	354.00	-	-

a. Regnault (ref. 104), 205-239; the table is adapted from that on 239.

The failure of comparability due to the behavior of glass was not merely a practical difficulty avoidable by specifying a certain type of glass as the standard glass. To do so, one would have needed to specify and control the exact chemical composition of the glass, the process of its manufacture, and the method of blowing the thermometer bulb. It would not have been possible to achieve the degree of precision wanted by Regnault in these procedures. In addition, the familiar vicious circularity would also have ruined any attempt to make empirical determinations of the behavior of glass as a function of temperature, since this would have required an already-trusted thermometer.

When he announced the incomparability of the mercury thermometer in 1842, Regnault was nearly prepared to endorse the air thermometer as the only comparable type. The thermal expansion of air being so great (roughly 160 times that of glass), the variations in the expansion of the glass envelope could be made negligible.¹²⁰ Still, Regnault was not comfortable. Refusing to grant any special status to gases, he demanded that the air thermometer, and gas thermometers in general, be subjected to a rigorous empirical test for comparability like all other thermometers.¹²¹

120. Regnault, "Sur la comparaison du thermomètre à air avec le thermomètre à mercure," *Annales de chimie et de physique*, 5 (1842), 83-104, on 103.

121. Regnault (ref. 104), 167.

Regnault had good reason to hesitate. He himself had shown that the coefficient of expansion varied according to the density even for a given type of gas. Perhaps the form of the law also varied? The variation in the coefficient was an annoyance, but there was no conceptual problem in graduating each thermometer individually so that it gave 100° at the boiling point of water. Variations in the *form* of the law would have negated comparability. Regnault considered it “absolutely essential” to submit this question to an experimental investigation.¹²²

To that end Regnault built constant-volume thermometers with gases of various densities, starting with atmospheric air. He rejected air thermometers that worked at constant pressure because they suffered from an inherent lowering of sensitivity at higher temperatures.¹²³ Each thermometer (figure 1a) consisted of a glass vessel (marked A) of capacity 700–800 cm³, placed in a bath of oil and connected to a mercury manometer consisting of glass tubes of inner diameter 12–14 mm. The apparatus started at temperature 0° (obtained by putting the vessel A into a bath of melting ice) and atmospheric pressure H (obtained by allowing free communication with the air). Then Regnault put A into a bath of an unknown higher temperature x , and noted h' , the reading of manometer connected to A, and H' , the barometer reading for atmospheric pressure at that point. The pressure within A was given as $H' + h'$. The ratio between $H' + h'$ and H indicated the temperature x , but not closely enough for Regnault. He made corrections based on the following considerations:

- The thermal expansion of glass is very small compared to the expansion of air, but it is still not negligible.
- Some air remains above the mercury in the manometer (in the space between point b and mercury level α , shown in figure 1b); this air will not be at the temperature x of the air in the vessel, but at some other temperature t , to be measured by a mercury thermometer placed near the manometer.
- Air remains in the glass tube connecting the vessel and the manometer (in the space between point a and point b in figure 1a); this air, too, will not be at the temperature x of the air in the vessel, but at some other temperature t' , to be measured by a mercury thermometer placed roughly at the midpoint of the tube.

Accordingly, Regnault expressed the weight W_1 of the air contained in the apparatus in the initial state as in equation (1) and the weight W_2 of air in the heated state as in equation (2). No air escapes the apparatus in the process of heating, so these weights must be the same. Equating (1) and (2), Regnault obtained x in terms of quantities directly measurable. The formulas are:

$$W_1 = \left[V + \frac{v}{1 + \alpha t} + \frac{v'}{1 + \alpha' t'} \right] \delta \frac{H}{760} \quad , \quad (1)$$

122. Ibid., 172.

123. Regnault (ref. 104), 168–171.

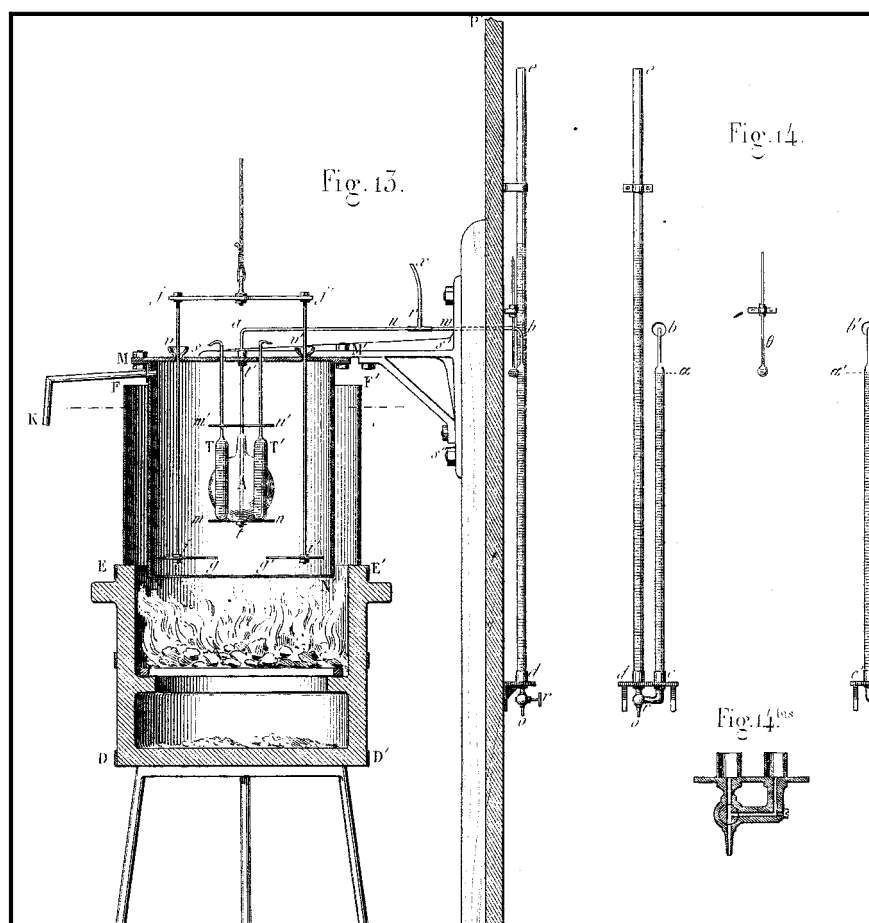


FIG 1. The constant-volume air thermometer used by Regnault. *Source:* Regnault, "Relations des expériences" (ref. 130), 168-171, figures 13 and 14.

where δ is the density of air at 0° and 760 mm of mercury. The factor $\delta H/760$ indicates the density of the air in the initial state (if Mariotte's law is assumed). The expression in parentheses is the effective volume of the air in the apparatus: V is the capacity of the vessel at 0° , v is the volume of air enclosed in the manometer, v' is the volume of the tube connecting the vessel and the manometer. The factors $(1 + \alpha)$, and $(1 + \alpha')$, are for calculating effective volumes at temperature θ , where α is the average coefficient of the thermal expansion of air under pressure H .

$$W_2 = \left[V \frac{1 + \kappa x}{1 + \alpha x} + \frac{v}{1 + \alpha} + \frac{v'}{1 + \alpha'} \right] \delta \frac{H}{760} \quad (2)$$

The symbol not yet explained, κ , is the mean coefficient of the vessel's thermal expansion. Regnault determined α case-by-case, adjusting its value to make sure that the thermometers being compared with each other would agree at 100° or near it.¹²⁴

Although Regnault made several assumptions, including Mariotte's law, in devising this procedure, they served only to help him construct and use the apparatus. The final judge of the reliability of the apparatus was the comparability of the results. He retained the assumptions because they produced a comparable apparatus. He gave no theoretical justification for them. Similarly, Regnault made use of mercury thermometers to get the temperature readings t and t' , and applied an average coefficient of expansion for air and glass (α and κ), when he knew that the thermometers were not reliable and expansions not exactly linear. Again these assumptions were only heuristic.

Typically Regnault placed two thermometers like *A* side by side in a bath of oil and recorded their readings at various points ranging from 0° to over 300° centigrade. The tests provided a relief. The data in Table 7, for instance, give a comparison of the readings of air thermometer *A*, whose “initial” pressure (that is, pressure at temperature 0°) was 762.75 mm of mercury, with the readings of *A'*, whose initial pressure was 583.07 mm.

Table 7. Regnault's comparison of air thermometers with different densities of air^a

Air thermometer <i>A</i>		Air thermometer <i>A'</i>		temperature difference (<i>A-A'</i>)
pressure (mmHg)	temperature reading (°C)	pressure (mmHg)	temperature reading (°C)	
762.75	0	583.07	0	0
1027.01	95.57	782.21	95.57	0.00
1192.91	155.99	911.78	155.82	+0.17
1346.99	212.25	1030.48	212.27	-0.02
1421.77	239.17	1086.76	239.21	-0.04
1534.17	281.07	1173.28	280.85	+0.22
1696.86	339.68	1296.72	339.39	+0.29

a. Regnault (ref. 104), 181.

The divergence between these two thermometers was always less than 0.3° in the range from 0° to 340°, and always below 0.1% of the magnitudes of the measured values. Moreover, the discrepancy between their readings was not systematic, but varied randomly. The results from other similar tests, with initial pressures ranging from 438.13 mm to 1486.58 mm, were similar. “One can therefore conclude with all certainty from the preceding experiments: the air thermometer is a perfectly comparable instrument even when it is filled with air at different densities.”¹²⁵

124. Ibid., 182-183.

125. Ibid., 181, 184, 185 (quote).

Regnault also made comparisons between the air thermometer and other gas thermometers and found that comparability held well between air and hydrogen, and also between air and carbonic acid gas. These gases had the same form of the law of expansion, though their coefficients of expansion were quite different from each other. However, as shown in Table 8, there were some serious and systematic discrepancies between air and sulfuric acid gas.

Table 8. Regnault's comparison of thermometers of air and sulfuric acid gas^a

Air thermometer A		Sulfuric acid thermometer A'		temperature difference (A-A')
pressure (mm Hg)	temperature reading (°C)	pressure (mm Hg)	temperature reading (°C)	
762.38	0	588.70	0	
1032.07	97.56	804.21	97.56	0.00
1141.54	137.24	890.70	136.78	+0.46
1301.33	195.42	1016.87	194.21	+1.21
1391.07	228.16	1088.08	226.59	+1.57
1394.41	229.38	1089.98	227.65	+1.73
1480.09	260.84	1157.88	258.75	+2.09
1643.85	320.68	1286.93	317.73	+2.95

a. Regnault (ref. 104), 186-188.

The generalized gas thermometer evidently would not be a comparable instrument. The air thermometer was enough: “[it] is the only measuring instrument that can be used with confidence for the determination of high temperatures; it is the only one that I will employ in the future, when the temperatures exceed 100°.”¹²⁶

Skeptical as he was about all suppositious regularities, Regnault's final pronouncement in favor of air was muted:¹²⁷

The simple laws accepted so far for the expansion of gases had led physicists to regard the air thermometer as a standard thermometer whose indications are really proportional to the increases in the quantities of heat. Since these laws are now recognized as inexact, the air thermometer falls back into the same class as all other thermometers, whose movement is a more or less complicated function of the increases in heat. We can see from this how far we still are from possessing the means of measuring absolute quantities of heat; in our present state of knowledge, there is little hope of finding by experiment simple laws in the phenomena that depend on these quantities.

Regnault had no patience with theoretical arguments designed to show that the

126. *Ibid.*, 259.
127. Regnault (ref. 120), 103-104.

expansion of air was uniform, and he was all too aware of the circularity involved in trying to demonstrate such a proposition experimentally. Even when he noted the comparability between the air, hydrogen, and carbonic acid thermometers and the deviation of the sulfuric acid thermometer from all of them, he was careful not to say that the former were right and the latter was wrong. He never strayed from the recognition that comparability did not imply truth.¹²⁸ In the end, what Regnault managed to secure was only a rather grim judgment that everything else was worse than the air thermometer.

Regnault's work on thermometry, like most of his experimental work, gained rapid and wide acceptance. His reasoning was impeccable, his technique unmatched, his thoroughness overwhelming. He did not back up his work theoretically, but he succeeded in avoiding theory so skillfully that there was no place that was open to any significant theoretical criticism. Thermometry as it had developed from De Luc was completed with Regnault's publication of the results on the comparability of gas thermometers in 1847. One year later the basic terms of debate would begin to shift radically and irreversibly, starting with the new theoretical definition of absolute temperature by the same William Thomson who had humbly made his pilgrimage to Regnault's laboratory. The landscape by the mid-1850s would become unrecognizably altered by the promulgation and acceptance of the principle of energy conservation, and subsequently by the powerful revival of the kinetic theory of heat.

Circularity

As long as we adhere to strict empiricism measurement will involve us in a circle. Some people have thought that making the circle wider would render it less vicious. In his argument regarding the theory-ladenness of observation, Pierre Duhem claimed that the physiologist had less to worry about than the physicist, because laboratory instruments were generally designed on the basis of the principles of physics. Hence, while the physiologist could proceed on the basis of a faith in physics, the physicist faced a crippling circularity in which he had to test the hypotheses of physics on the basis of those same hypotheses.¹²⁹ To take more recent examples, we could understand in a similar vein Ian Hacking's argument for the reality of microscopic structures seen to be the same through different microscopes, and Peter Kosso's argument that empirical testing is better when the assumptions that form the basis of the test are more independent from the assumptions that are being tested and the theory to be tested by the observation produced by the instrument.¹³⁰ The best we can and should hope for is an agreement between

128. Regnault (ref. 104), 165-166.

129. Pierre Duhem, *The aim and structure of physical theory*, trans. Philip P. Wiener (New York, 1962), 180-183 (text of 1906).

130. Ian Hacking, *Representing and intervening* (Cambridge, 1983), 200-202; Peter Kosso, "Dimensions of observability," *British journal for the philosophy of science*, 39 (1988),

many sources. Each of them might be fallible, but it would stretch plausibility for all of them to be false in exactly the same way.

It may seem that Regnault's testing by comparability was also a strategy to argue for the truth of a result by showing its agreement with results obtained by other methods since he sought to show whether variants of a given type of thermometer agreed in their readings. However, for Regnault comparability did not amount to truth, even approximately or probably; it only meant self-consistency for a given type of instrument. Since it would not have been possible to test comparability for all potentially relevant parameters, only a clear *failure* of comparability was useful; that allowed Regnault to eliminate an instrument as a candidate for indicating true temperatures.

In this falsificationist mode, Regnault's strategy was precisely the opposite of that adopted by those who would loosen the logical circle. He wanted to tighten it. In testing the comparability of thermometers Regnault was checking the self-consistency of the assumption that a certain substance expanded linearly with temperature. For the failure of comparability to be an unequivocal verdict against that assumption, Regnault needed to eliminate all other assumptions that could be blamed for the failure. If auxiliary hypotheses interfere with the logic of falsification, it is best to get rid of them altogether. This Regnault managed beautifully. When De Luc argued that the expansion of liquids other than mercury was not linear, he relied on the auxiliary assumption that the specific heat of water was constant. Regnault's way of proceeding left no room for attacks against auxiliary hypotheses. Tightening the circle, in the sense of involving fewer assumptions, made the refutation more decisive. Sometimes there is virtue in circularity.

Like all strategies, however, Regnault's strategy worked only because it was applied in appropriate and fortunate circumstances. Had it turned out that none of the available types of thermometers were comparable enough, temperature measurement as he conceived it would have been impossible. Had it turned out that a number of thermometer-types had similar and reasonable degrees of comparability, the criterion would not have had much discriminating power. Scientific inquiry takes place in a great variety of circumstances, and we cannot expect any rule or strategy to be effective in all circumstances.