

DULONG AND PETIT: A CASE OF DATA FABRICATION?⁽¹⁾

Carmen J. Giunta, Le Moyne College

Introduction

The famous law of Dulong and Petit was based upon their own specific heat data first reported in 1816. For at least 15 years there has been public expression of doubt about the reliability of their data, however. Peter Macinnis spoke on this subject on a radio program of the Australian Broadcasting Corporation during the 1980s (2), and Paul Schwarz published a letter in *Chemical and Engineering News* in 1987 (3). Much of what follows is an elaboration of their work for a scholarly audience. I propose to examine the data, compare it to modern data, and develop reasons for questioning their numbers. The inference can reasonably be drawn that they fabricated some of that data; obviously, however, no one who really knows has an opportunity to testify.

Brief Biographical Sketches

Pierre-Louis Dulong was born in Rouen in 1785. Orphaned at the age of 4, he was raised by an aunt. He entered the *École Polytechnique* in Paris in 1801 but withdrew from it in his second year. He practiced medicine for a time, but he eventually ran out of money in that occupation. He turned next to botany and then to chemistry, working with Thenard and then Berthollet. He held teaching posts at the *École Normale* and then the *École Vétérinaire d'Alfort*. In the early 1810s, Dulong discovered nitrogen trichloride, whose explosiveness cost him a finger and the sight in one eye. He began working with Petit in 1815, a collaboration that led to three papers on heat, of which the paper announcing the law of constant atomic heats in 1819 was the

last. Dulong was appointed Professor of Chemistry at the *Faculté des Sciences* in Paris in 1820. That same year he was appointed Professor of Physics at the *École Polytechnique*—a post vacated by the premature death of Petit. After Petit's death Dulong continued to work on heat, including the specific heat of gases. He was appointed to the physics section of the *Académie des Sciences* in 1823, serving as president in 1828. He died in Paris in 1838 (4).

Alexis-Thérèse Petit was born in Vesoul in 1791. He was a prodigious student, satisfying the entrance requirements for the *École Polytechnique* before age 11; he enrolled there at age 16 (the minimum permissible age). He graduated first in his class—in a class by himself, actually; for he placed “before the line” so that the next student was designated “first.” He was first Professor of Physics at the *Lycée Bonaparte* in Paris and then at the *École Polytechnique* in 1815. He died in 1820 from tuberculosis, which he had contracted in 1817 (5).

The Law: Its Reception and Subsequent Use

The first joint paper by Dulong and Petit in 1816 treated the expansion of materials important to thermometry, such as mercury (6). Their paper the following year (7) on the expansion of gases and mercury and on cooling earned them a 3000-franc prize from the *Académie des Sciences* (8). In the course of this investigation, they measured several specific heats over a wide range of temperatures. In their third paper (1819) they announced the law of constant atomic heat capacities and discussed some theoretical questions concerning heats of reaction

(9). Because this paper figures so prominently in the following analysis, I will refer to it below as “the” DP paper, data from it as the DP data, etc.

The table from this paper is reproduced as Table I. It contains a column of specific heats (on a scale in which water is unity), a column of atomic weights (on a scale in which oxygen is unity), and a column containing the product of the first two. The product, as noted in the paper, is significant because it represents the heat capacities of the atoms. The numbers in that product column are strikingly similar indeed. As the authors state, “The simple inspection of these numbers exhibits an approximation too remarkable by its simplicity not to immediately recognize in it the existence of a physical law capable of being generalized and extended to all elementary substances. ... The atoms of all simple bodies have exactly the same capacity for heat.”

The law was never established to be quite so general or exact as Dulong and Petit presented it (10). Indeed, the law proved to be only approximate. For one

thing, several nonmetals have atomic heat capacities that deviate from the law. For another, heat capacities are temperature-dependent, with different temperature dependencies—a criticism of the law that dates back at least to John Dalton (11).

At the time of Dulong’s death, the law was not even mentioned in one short summary of his work (12), but it was to receive more attention and prominence later on. Stanislao Cannizzaro’s “Sketch of a Course in Chemical Philosophy” (13), which was widely influential in establishing a consistent set of atomic weights and formulas, made extensive use of “the law of the specific heats of elements and of compounds.” Statistical me-

chanics eventually provided an explanation as to why the law holds even approximately at relatively high temperatures, and its breakdown at low temperatures was explained through the use of quantum mechanical energy expressions in statistical thermodynamic treatments (14).

Data Fabrication

1. Suspicions

Suspicions of data fabrication arise if one compares the DP data table to a corresponding table of modern values. Assembling a set of modern data for comparison,

however, is not as straightforward as one might guess. Any number of contemporary reference books and textbooks contain molar heat capacities of the elements at 25°C. Dulong and Petit, however, reported that they measured their heat capacities by cooling samples in ice water from a temperature 5-10° above the temperature of that medium. *The International Critical Tables* (15) are a convenient (if rather old) source

of temperature-dependent heat capacities, and I have employed 0°C values from that source. Allotropism is an additional complicating factor in making a comparison to modern data. Two elements on the DP list have two common forms, whose molar heat capacities differ by 1-2 J K⁻¹ mol⁻¹. Tin has a gray α and a white β form. The gray form is thermodynamically more stable at 0°C. The transition temperature is 13°C (16), so the white form is the standard state at the commonly used reference temperature of 25°C. Sulfur also has two forms, rhombohedral α and monoclinic β . The rhombohedral form is the standard state of the element at both 0°C and 25°C, as the transition temperature is about 93°C (16). In the tables below the heat capacities of the thermody-

TABLE 1. Table from Petit and Dulong 1819 (9)

Element	Specific heats	Relative weights	Products of the weight of each atom by the corresponding capacity of the atoms
Bismuth	0.0288	13.30	0.3830
Lead	0.0293	12.95	0.3794
Gold	0.0298	12.43	0.3704
Platinum	0.0314	11.16	0.3740
Tin	0.0514	7.35	0.3779
Silver	0.0557	6.75	0.3759
Zinc	0.0927	4.03	0.3736
Tellurium	0.0912	4.03	0.3675
Copper	0.0949	3.957	0.3755
Nickel	0.1035	3.69	0.3819
Iron	0.1100	3.392	0.3731
Cobalt	0.1498	2.46	0.3685
Sulfur	0.1880	2.011	0.3780

namically stable form at 0°C for both tin and sulfur are used. Although this is a natural, perhaps even canonical, choice, it is nevertheless arbitrary, because Dulong and Petit did not provide any descriptions of their samples. Fortunately, the statistical analyses presented below do not depend a great deal on this selection, as will be discussed below.

Table 2 displays the product of atomic weight and specific heat, the quantity that Dulong and Petit correctly interpreted as an atomic heat capacity, the constancy of which is the law that they announced in 1819. The DP atomic heat capacities differ from modern values by no more than 10% in either direction; the DP value for sulfur is 10% greater than the modern value, the largest error. The DP molar heat capacities are remarkably constant—a bit too constant, in fact. The range of the DP data (difference between largest and smallest value) is only 1.04 J mol⁻¹, compared to 3.19 for the modern data. The range is the most obvious, if not the most telling, measure of variability, a subject to be explored more rigorously below. For now it is worth considering the question of how one can obtain such low variability in a set of data based on measurements that presumably have larger errors than modern data.

Table 3 displays DP atomic weights in modern atomic mass units (amu, where ¹²C = 12) and the corresponding modern atomic weights. The DP atomic weights of platinum, tellurium, and cobalt are anomalously low, by 9%, 49% and 33% respectively. All other values vary by less than 4% from the modern figures. Large atomic weight errors are understandable for tellurium and cobalt, because the determination of atomic weights was dependent on chemical analyses as well as on assumptions about formulas. From accurate analytical data on TeO₂, one would obtain an atomic weight half the true value for tellurium if the analyte was believed to be TeO. Similarly, an atomic weight two-thirds of the true value for cobalt would be inferred from accurate analytical data on CoO if it was believed to be

TABLE 2. Atomic heat capacity at 0°C (J K⁻¹ mol⁻¹)

Element	DP (9)	modern (15)
Bismuth	25.64	25.41
Lead	25.40	26.19
Gold	24.80	25.44
Platinum	25.04	25.71
Tin*	25.30	4.5
Silver	25.16	25.11
Zinc	25.01	25.10
Tellurium	24.60	25.58
Copper	25.14	24.33
Nickel	25.56	25.34
Iron	24.98	24.51
Cobalt	24.67	24.40
Sulfur*	25.30	23.0

*allotropes: see text

Co₂O₃. The assumptions employed in atomic weight determinations were arbitrary and were recognized to be so by at least some chemists of the time, including Dulong and Petit (17). Therefore, the deviations of the tellurium and cobalt atomic weights from modern values are understandable and justifiable. The same can be said for the fact that DP used different atomic

weights than the most recent ones reported by Berzelius, a fact noted by several writers (8, 18, 19, 20). The atomic weight of platinum may well be a misprint, as several authors have commented. In any event, the DP atomic heat capacity of platinum is not equal to the product of the numbers that appear in the atomic weight and specific heat columns. (See discussion below.) Otherwise, there is nothing obviously improper about the reported atomic weights.

TABLE 3. Atomic weight (amu, ¹²C = 12)

Element	DP	modern (16)
Bismuth	212.79	208.98
Lead	207.19	207.2
Gold	198.87	196.967
Platinum	178.55	195.08
Tin	117.60	118.71
Silver	108.00	107.868
Zinc	64.48	65.39
Tellurium	64.48	127.6
Copper	63.31	63.546
Nickel	59.04	58.69
Iron	54.27	55.847
Cobalt	39.36	58.933
Sulfur	32.17	32.066

TABLE 4. Specific heat ($\text{J g}^{-1} \text{K}^{-1}$)

Element	DP	modern (21)	DP – modern
Bismuth	0.1205	0.1216	-0.0011
Lead	0.1226	0.1264	-0.0038
Gold	0.1247	0.1292	-0.0045
Platinum	0.1314	0.1318	-0.0004
Tin	0.2151	0.206	0.009
Silver	0.2330	0.2328	0.0003
Zinc	0.3878	0.3839	0.0040
Tellurium	0.3816	0.2005	0.1811
Copper	0.3971	0.3829	0.0142
Nickel	0.4330	0.4318	0.0013
Iron	0.4602	0.4389	0.0214
Cobalt	0.6268	0.4140	0.2127
Sulfur	0.7866	0.717	0.069

Table 4 displays DP specific heats expressed in modern units of $\text{J g}^{-1} \text{K}^{-1}$, the corresponding modern data (21), and the difference between them. Note that Dulong and Petit reported that they measured specific heats of several solids by a method of cooling. They described the method involving cooling of the experimental samples and a standard through a common temperature range, in this case from 5-10°C to 0°C. It is indeed a valid method (22). Rates of cooling through a given temperature range are directly proportional to the heat capacity of the cooling body. Dulong and Petit would have preferred to use an ice or water calorimeter; however, they said that the samples they had were not large enough (less than 30 g) for such methods to yield precise data. Their paper described the apparatus in some detail, including an accurate and finely graded thermometer good to 1/200th of a degree. They did not give a formula that related specific heat to their measurements, though, because the many correction terms would take them too far afield (9).

The DP specific heats of tellurium, cobalt, and sulfur are anomalously high, by 90%, 51%, and 10%, respectively. All other values fall within 5% or less of modern figures. The first suspicious observation is that the largest errors in both specific heat and atomic weight are in the same elements, tellurium and cobalt. The errors in specific heat are large ones, and the property is based solely on mass and temperature measurements, independent of the arbitrariness that attended atomic weights and atomic formulas. Furthermore, the large

errors in both elements compensate the atomic weight errors such that the product of atomic weight and specific heat is very nearly the same as for the rest of the elements in the table. The improbability of independent compensating errors is the main assertion made previously by both Paul Schwarz (3) and Peter Macinnis (2).

2. Statistical Analysis

The law Dulong and Petit proposed was literally too good to be true. In one sense, that fact has been well known for a long time: the law holds only approximately. The data on which the law was based are also too good to be true, as the following analyses suggest.

The variance is a statistical measure of the variability of data within the data set, a much more telling measure than the range. The sample variance, s^2 , is defined as the sum of the squares of the differences between each data point and the mean of the data set. For the 13 DP atomic heat capacities, the sample variance is less than one sixth as great as the variance among modern values for the same elements (0.102 vs. 0.670). A statistical test known as the F test may be used to compare variances of two samples, to assess the probability that the samples were drawn from populations with the same variance (23). The test statistic is the ratio of the sample variances:

$$F = \frac{s_1^2}{s_2^2}$$

where $s_1 > s_2$. The computed F value (6.58) exceeds the critical value for the 0.5% significance level for 13 observations per sample (4.91), supporting the hypothesis that the variance of the modern values is really greater than that of the DP data set. That is, the test strongly suggests that the DP data and the modern data do not reflect measurements of the same quantities with randomly distributed errors (24).

By themselves, the variance data are suggestive. It is difficult to imagine how data based on measurements that a modern observer would expect to be cruder than modern measurements could legitimately lead to a smaller sample variance than modern data. This anomalously small variance in the DP atomic heat capacities, however, is even more dubious when combined with the large errors in DP specific heats.

If the DP specific heats were measured by a valid

method without systematic error, one would expect the deviations of the DP values from the true values to be randomly distributed with a normal distribution. Specific heat errors are displayed in Table IV. They are plotted in Figure 1 on a normal or Gaussian scale. If the data points were normally distributed, they would fall along a straight line. Clearly these points do not. A statistical test of the hypothesis that the errors were randomly taken from a normal distribution indicated that they were not, with a significance level of less than 0.1%.

The errors for cobalt and tellurium are suspiciously large (as Macinnis and Schwarz had previously pointed out). Combined with the fact that they compensate errors in atomic weight (however legitimate) to yield atomic heat capacities with anomalously low dispersion stretches credulity past the breaking point. The DP data are truly stuck on the horns of an improbability dilemma: it is difficult to escape the conclusion that Dulong and Petit made up at least some of the specific heats they claim to have measured.

One additional way to see that Dulong and Petit used specific heat data that are not particularly accurate to obtain atomic heat capacities that are remarkably constant is to compare the average error in specific heat to the average deviation in DP atomic heat capacities. That is, for each element, compute the absolute value of the error in specific heat c , and divide it by the true value of the specific heat: –

$$\frac{|c(\text{DP}) - c(\text{modern})|}{c(\text{modern})}$$

The mean of these specific heat errors is 13.3% for the whole set of 13 elements, and it is still 2.9% when cobalt and tellurium are excluded. Now for each element, compute the absolute value of the deviation of DP atomic heat capacities from their mean value, and divide it by that mean atomic heat capacity:

$$\frac{|C(\text{DP}) - \langle C(\text{DP}) \rangle|}{\langle C(\text{DP}) \rangle}$$

The mean of these deviations is just 1.0%.

As mentioned above, the selection of modern data to be used for comparison to DP data is somewhat arbitrary. The computations carried out above employed the heat capacities of the thermodynamically stable form at 0°C for both tin and sulfur, the two elements that have two allotropes. In the case of tin, the 0°C allotrope (gray) has a heat capacity closer to the DP value than the less stable one (white); in the case of sulfur, the 0°C allotrope (rhombohedral) has a heat capacity further from the DP value than the less stable one (monoclinic). Giving the DP data the benefit of a doubt by using the modern data that are closer to those DP data (i.e., keeping the more stable form of tin and using the less stable form of sulfur) still leads to a strong conclusion of fraud.

Using an atomic heat capacity of 24.0 J mol⁻¹ K⁻¹ (instead of 23.0) and a specific heat of 0.748 J g⁻¹ K⁻¹ (instead of 0.717) for sulfur does indeed reduce the range (to 2.19, compared to 3.19) and variance (to 0.419, compared to 0.670) of the modern atomic heat capacities. (After all, sulfur was, and remains, the element with the lowest atomic heat capacity.) The F statistic becomes 4.11, no longer significant at the 0.5% level, but still significant at the 2.5% level. The assertion that atomic heat capacities are just too constant is still a probable

one, but one which cannot be asserted with quite the same level of confidence. The other horn of improbability, however, is even stronger with this choice of modern data. With the modern atomic and specific heat capacities for sulfur more in line with the rest of the DP data, the DP specific heats of tellurium and cobalt stand out as all the more anomalous. The distribution of specific heat errors is still not normal. The error of

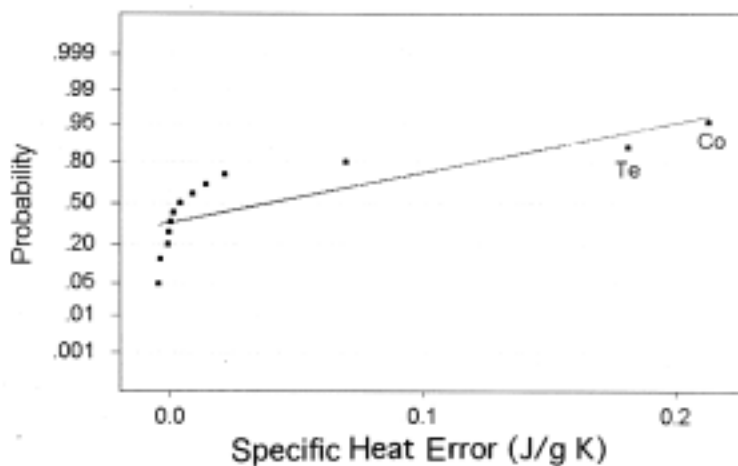


Figure Normal probability plot of errors in DP specific heat. The plotted points are distributed along the horizontal axis as the actual errors are distributed and along the vertical axis as normally distributed errors. If the actual errors were normally distributed, they would fall approximately along a straight line.

specific heat for tellurium is more than 13 standard deviations away from the mean error defined by the other 11 data points; that of cobalt is nearly 16 standard deviations away. How such specific heat outliers can lead to atomic heat capacities even as constant as the modern data (let alone even slightly more constant) is inexplicable.

To test the robustness of the statistical conclusions, I used yet one more set of modern data, a tabulation of heat capacities of the elements at 25°C and 1 bar (25). Although there are good reasons to believe that this set of data is less appropriate as a reference set than the previous ones (mainly because of the different temperature), it is worthwhile to see whether such a perturbation in the reference data alters the statistical conclusion. These room-temperature data have slightly different heat capacities because of the temperature difference, and they reflect yet another selection of allotropes, white tin and rhombohedral sulfur. The DP atomic heat capacities still have a smaller variance than the reference data ($F = 10.9$, significant at 0.5% level). The distribution of specific heat errors is still not normal. The error of specific heat for tellurium is more than seven standard deviations away from the mean error defined by the other 11 data points; that of cobalt is more than eight standard deviations away.

3. Discussion

It is natural to speculate: (a) that Dulong and Petit concluded the atomic heat capacity was constant, either empirically on the basis of fewer elements than they listed or theoretically, and (b) that they computed specific heats consistent with their law and with their best estimates of atomic weights for at least some of the elements in their table, including tellurium and cobalt. Is there any evidence to support this speculation? Is there any way of knowing whether tellurium and cobalt were the only two pieces of fabricated data? Are there ways to explain the data without fabrication of specific heat data (including fabrication or biased selection of atomic weight data)? Carrying out the F test without data on tellurium and cobalt still suggests that the DP data are too good to be true. In other words, tellurium and cobalt appear certainly fraudulent, because they neatly compensate large errors in atomic weight, but other specific heats appear to have been chosen to give a product of specific heat and atomic weight close to the constant value as well. (The F statistic for the 11 data points without cobalt or tellurium is 11.2, still much greater than the critical value of 5.85 (0.5% significance level,

one-tailed test) (26). Which other data were made up, however, is not obvious.

Dulong and Petit had reported specific heats of several substances in their 1817 paper concerned primarily with thermometry and cooling laws (7). In that paper, they reported specific heats measured over a wide range of temperatures by the method of mixtures (plunging a sample into a liquid of known specific heat). Interested in the variation of specific heat with temperature, they reported mean specific heats for the ranges 0-100°C and 0-300°C for seven elements. Five of these (iron, zinc, silver, copper, and platinum) would later appear in the table of data on which the Dulong and Petit law was based; the other two were mercury and antimony. One might guess that Dulong and Petit formulated their law on the basis of these specific heats and then fabricated some of the others; however, this is simply speculation (27).

Three of the elements (copper, zinc, and silver) listed in both papers have identical specific heats to four figures, which is in itself rather suspicious. After all, the 1819 values were measured by the method of cooling over a temperature range reported to be at most 0-10°C; the 1817 values were measured by the method of mixtures over a temperature range reported to be 0-100°C. The absolute agreement to four figures of two methods at two slightly different temperature ranges is suspicious, particularly in light of the quite notable temperature differences reported in the 1817 paper: specific heats at 0-100°C were some 5-10% lower than those reported for 0-300°C. Perhaps Dulong and Petit did not measure the specific heats of these elements again in 1819 by the method described. A fourth element, iron, has only a minuscule difference in specific heats (0.2%) between the two papers. The fifth element common to both papers, platinum, raises additional questions.

The comedy of errors surrounding the platinum data makes it very difficult to judge whether fraud, or simply carelessness, was at work. In the 1819 paper the numbers printed for platinum do not "add up;" the actual product of the printed specific heat (0.0314) and atomic weight (11.16) is 0.3504, not 0.3740 as printed. Because the printed value of 0.3740 is clearly in the narrow range of atomic heat capacities listed by Dulong and Petit, whereas the actual product would be a serious outlier (more than five standard deviations away from the mean of the remaining atomic heat capacities), it is fairly clear that the product is printed correctly and that one of the factors was misprinted. Which factor? That

the atomic weight of platinum is a misprint has been proposed by several authors, for the printed 11.16 is close to, but not a simple multiple of, Berzelius' 1818 atomic weight of 12.15. But the product of specific heat 0.0314 and putative atomic weight 12.15 is 0.3815, not the printed 0.3740. If 11.16 were a misprint, then, it would have to be a misprint for $0.3740/0.0314 = 11.91$. Could a printer's error have rotated the digits 16 into 91 (28)? It is also possible that the specific heat is the misprinted factor, and that the intended specific heat was $0.3740/11.16 = 0.0335$. A transcription error of 0.0314 for 0.0335 is plausible when one notes that the number directly below the specific heat of platinum is that of tin, 0.0514. Jan van Spronsen found additional provenance for the figure 0.0335 in a German translation of the 1817 paper of Dulong and Petit (which he cited as *J. Chem. Phys. (Schweigger)* 1819, 25, 304); the French original has 0.0355 instead. Van Spronsen asserted that the German translation had the correct value, and that the original French publication had 0.0355 as a misprint (19). Although the profusion of misprints sounds improbable, I propose two additional reasons for believing van Spronsen was correct. First, in the 1817 paper (French version), platinum was the only substance listed as having an identical specific heat over the 0-100°C and 0-300°C ranges; although the specific heat of platinum does, in fact, have a weaker temperature dependence than the other elements studied in the 1817 paper, it is not much smaller than that of silver and copper, for which Dulong and Petit reported different specific heats over the different temperature ranges. Therefore, it is quite likely that the specific heat measured for platinum in 1817 over either 0-100° or 0-300° was not the printed value of 0.0355. Second, we have already seen Dulong and Petit recycle specific heats from their 1817 paper in their 1819 paper (29).

This detailed scrutiny of the figures reported for platinum leaves unanswered (so far) the question of the provenance of the atomic weight (whether we take it to be 11.16 or 11.91), which is not simply related to published atomic weights available at the time. In light of the suspicion of fabrication already cast, is it not reasonable to guess that the atomic weight was fabricated, obtained by dividing 0.3740 by the measured specific heat (0.0335 or 0.0314)?

If so, another question must be raised—one that ought to be brought up in any event.

Is it possible that Dulong and Petit actually measured specific heats and simply adjusted atomic weights or even selected atomic weights (from a variety of published sources) with a bias that led to the constancy of atomic heat capacities? Note that I am not referring here to arbitrary factors of small-integer ratios mentioned above, but to atomic weights based on assorted chemical analyses published by different investigators.

At first blush, this appears to be a promising alternative. After all, platinum seems to be an example of atomic weight fabrication or selection. Furthermore, the DP paper explicitly stated that they measured specific heats, including a detailed description of how they did so, whereas it said next to nothing about sources of their atomic weight data. Dulong and Petit stated that published specific heats then available were highly unreliable, showing great variation from one experimenter to another, and including values "three or four times as great as they ought to be" (9). Surely they would not have made such pointed remarks about the measurement of specific heats if they had fabricated specific heats.

Upon further examination, however, the hypothesis of atomic weight fabrication or biased selection must fall. For one thing, notwithstanding their statements to the contrary, Dulong and Petit recycled some specific heat measurements from a previous paper, despite their descriptions of method and apparatus. More conclusively, it is quite clear that Dulong and Petit used a single set of atomic weights (based on analyses published in 1818 by Berzelius (30)), with the apparent exception of

TABLE 5. Atomic weight ($O = 1$)

Element	DP	Berzelius (30)	Berzelius/DP
Bismuth	13.30	17.738	1.334
Lead	12.95	25.8900	1.999
Gold	12.43	24.8600	2.000
Platinum	11.16	12.1523	1.089
Tin	7.35	14.7058	2.001
Silver	6.75	27.0321	4.005
Zinc	4.03	8.0645	2.001
Tellurium	4.03	8.0645	2.001
Copper	3.957	7.9139	2.000
Nickel	3.69	7.3951	2.004
Iron	3.392	6.7843	2.000
Cobalt	2.46	7.3800	3.000
Sulfur	2.011	2.0116	1.000

platinum, as the basis for their atomic weights (31). Table V displays the DP atomic weights and the 1818 Berzelian atomic weights and their ratios; with the exception of platinum, the ratios are those of small integers to at least three significant figures. Dulong and Petit may have selected the small-integer ratios to make the law work (32); however, they did not search for atomic weights that narrowed the variation among their atomic heat capacities.

Historiography of the Dulong and Petit Law

Why was this alleged fabrication undetected for so long? First of all, it is not surprising that it escaped detection of Dulong and Petit's contemporaries. Accurate atomic weights and specific heats were not available at the time. (Indeed, one can find the DP specific heats for cobalt and tellurium in a textbook published more than 20 years later (33)!) Furthermore, the statistical concept of variance and inferential statistical tests such as the F test were not yet available either. Although the accuracy of the Dulong and Petit law was questioned and tested since its announcement, the provenance of the data was not.

Two history of science papers from the 1960s involved the Dulong and Petit law: Robert Fox, "The Background to the Discovery of Dulong and Petit's Law" (8) and Jan van Spronsen, "The History and Prehistory of the Law of Dulong and Petit as Applied to the Determination of Atomic Weights" (19). In neither case did the authors suspect Dulong and Petit of data fabrication. Although both provided valuable insights, including leads relevant to this paper, there are, naturally, some conclusions in these papers incompatible with data fabrication.

In particular, Fox begins his paper by examining a story told by Jean-Baptiste Dumas that Dulong and Petit were pushed into announcing their law by a "calculated indiscretion" of François Arago, Petit's brother-in-law. Fox was initially skeptical of this account, told 60 years after the fact solely by someone (Dumas) who was not there. Fox concluded, however, that the account was essentially substantiated, that the Dulong and Petit law was indeed unexpected and not part of a deliberate program of research. Of course, a fabricated result cannot be unexpected, so the present work is clearly contradictory to Fox on this point. On the other hand, pressure to announce the law hastily could have provided a motive for data fabrication.

Van Spronsen makes note of the compensating errors in the DP specific heat and atomic weight of tellurium, stating that Dulong and Petit found an inaccurate value for the specific heat, which led them to elect an atomic weight value half of the true value.

Slightly earlier, Gates wrote a brief note to the *Journal of Chemical Education* on Dulong and Petit, responding to a paper on the development of calorimetry (18). His letter clearly identifies the source of the DP atomic weights; however, it is less perceptive about suspicious data, speaking of compensating errors (about platinum in this case). More than 20 years later, when Schwarz discovered "at least, a bit of wishful thinking" in their results, Gates wrote another letter defending Dulong and Petit, who, he said, simply adjusted the atomic weights of cobalt and tellurium, as they had adjusted many other atomic weights, by small-integer ratios. In these cases, however, the adjustment was wrong because it was "based on grossly inaccurate specific heat measurements" (34).

Schwarz was researching relationships among atomic heat capacities, a subject upon which he reported to the Chemical Education division at the Spring 1986 National Meeting of the American Chemical Society. The currency of the topic of cheating in research prompted him to write a letter to *Chemical and Engineering News* the following year in which he reported the suspicious tellurium and cobalt data (3). To the best of my knowledge, this letter is the first and only accusation of fraud that has appeared in the chemical literature.

Meanwhile Macinnis, an Australian science writer and educator, noted and discussed the fabrication of some of the DP data on the Australian Broadcasting Corporation radio program "Ockham's Razor." That program was included in a book of scripts from the show. Macinnis has repeated the tale for a computer list on fraud in science, and in personal correspondence to the author (35).

Macinnis told me that the fabrication had been noted in print, somewhere around 1985, he thought, possibly in the *Journal of Chemical Education*. I have not been able to find such a paper (except for Schwarz's letter) in either the chemical literature or the history of science literature. I made an informal inquiry to the history of chemistry internet list (CHEM-HIST) for leads on the possible "fudging" of data by Dulong and Petit. The only responses I received mentioned the adjustment of

atomic weights by small-integer ratios. I am, therefore, left with the impression that the insights of Macinnis and Schwarz have not penetrated the history of science community because of where those insights appeared.

Conclusion

At least some of the data upon which Dulong and Petit based their law of constant atomic heat capacity appears to have been fabricated. In particular, the specific heats of cobalt and tellurium, which Dulong and Petit state they measured, appear to have been fabricated. Other specific heats may have been fabricated as well, or at least recycled from an earlier publication that was supposed to have involved a different measurement method and temperature range. Any suspicion of data fabrication seems to have gone unnoticed, or at least unreported, until the middle 1980s; and it has not appeared in a scholarly publication until the present article.

ACKNOWLEDGMENTS

Thanks to Peter Macinnis and Paul Schwarz for insightful comments and information and to William Rinaman and one of the referees for advice and assistance on the statistical analyses.

REFERENCES AND NOTES

- Presented as "Dulong and Petit: a Case of Scientific Misconduct?" at the 221st National American Chemical Society Meeting, San Diego, CA, April 3, 2001, HIST 015.
- Peter Macinnis first told this tale in about 1985 on "Ockham's Razor," a radio program of the Australian Broadcasting Corporation.
- P. Schwarz, *Chem. Eng. News*, June 15, 1987, 3, 44.
- M. P. Crosland, "Dulong, Pierre Louis" in C. C. Gillispie, Ed., *Dictionary of Scientific Biography*, Charles Scribner's Sons, New York, 1970-1980, Vol. 4, 238-242.
- R. Fox, "Petit, Alexis Thérèse" in C. C. Gillispie, Ed., *Dictionary of Scientific Biography*, Scribner, New York, 1970-1980, Vol. 10, 545-546.
- P.-L. Dulong, A.-T. Petit, "Recherches sur les lois de dilatation des solides, des liquides et des fluides élastiques, et sur la mesure exacte des températures," *Ann. Chim. Phys.*, **1816**, 2, 240-263.
- P.-L. Dulong, A.-T. Petit, "Researches on the Measure of Temperatures, and on the Laws of the Communication of Heat," *Ann. Chim. Phys.*, **1817**, 7, 113-154, 225-264, 337-367; English translation in *Ann. Philos.*, **1819**, 13, 112-124, 161-182, 241-251, 321-339.
- R. Fox, "The Background to the Discovery of Dulong and Petit's Law," *Br. J. Hist. Sci.*, **1968**, 4, 1-22.
- A.-T. Petit, P.-L. Dulong, "Recherches sur quelques points importants de la Théorie de la Chaleur," *Ann. Chim. Phys.*, 1819, 10, 395-413; English translation in *Ann. Philos.*, **1819**, 14, 189-198.
- R. Fox, *The Caloric Theory of Gases from Lavoisier to Regnault*, Clarendon Press, Oxford, 1971, 282.
- J. Dalton, *A New System of Chemical Philosophy*, 2, Manchester, 1827.
- Duke of Sussex, [Address Delivered before the Royal Society], Abstracts of the Papers Printed *Philos. Trans. R. Soc. London*, 1837-1843, 4, 84-109.
- S. Cannizzaro, *Nuovo Cimento*, **1858**, 7, 321-366, translated as Alembic Club reprint, #18 and posted at <http://dbhs.wvusd.k12.ca.us/Chem-History/Cannizzaro.html>.
- See, for example, R. K. Fitzgerald, F. H. Verhoek, "The Law of Dulong and Petit," *J. Chem. Educ.*, **1960**, 37, 545-549.
- L. Rolla, G. Piccardi, "Heat Capacity of Solid and Liquid Elementary Substances above 0°C," *International Critical Tables*, McGraw-Hill, New York, 1929, Vol. 5, 92-94.
- J. Emsley, *The Elements*, Oxford University Press, Oxford, 1989.
- In the DP paper (Ref. 9), they noted: "As no precise method exists of discovering the real number of atoms of each kind which enter into a combination, it is obvious that there must always be something arbitrary in the choice of the specific weight of the elementary molecules; but the uncertainty can be only in the choice of two or three numbers which have the most simple relation to each other."
- H. S. Gates, *J. Chem. Educ.*, **1964**, 41, 575.
- J. W. Van Spronsen, "The History and Prehistory of the Law of Dulong and Petit as Applied to the Determination of Atomic Weights," *Chymia*, **1967**, 12, 157-169.
- A. J. Ihde, *The Development of Modern Chemistry*, Harper & Row, New York, 1964; Dover Publications, New York, 1984.
- Obtained by dividing molar heat capacities tabulated above by modern molar masses.
- See R. L. Weber, *Heat and Temperature Measurement*, Prentice-Hall, New York, 1950, for a procedure for measurement of specific heat by the method of cooling.
- D. J. Sheskin, *Handbook of Parametric and Nonparametric Statistical Procedures*, CRC Press, Boca Raton, FL, 1997, 159-164, 690-693. If $F \geq F_{\text{critical}}$ for a given significance level α , then the probability that the DP variance is not really smaller than the modern variance is $\leq \alpha$. The significance level refers to a one-tailed F test, which is appropriate for evaluating the hypothesis that the variance of the modern data exceeds that of the DP data. If the hypothesis were simply that the variances

- were unequal, a two-tailed test would be appropriate, and the quoted critical value would represent a 1% confidence level (0.5% at each end of the distribution).
24. One of the assumptions behind the F test is that the two data sets are normally distributed about their means. Both sets of data were tested for normality, and they are satisfactory with respect to this condition. Moreover, a nonparametric test of variances, Levene's test, supports the conclusion that the DP variance in atomic heat capacities is really smaller than the modern variance at a 2% significance level.
 25. D. R. Lide, Ed., *CRC Handbook of Chemistry and Physics*, 75th ed., CRC Press, Boca Raton, FL, 1995.
 26. Even with the "benefit of the doubt" modern data for sulfur, the F test is significant at the 0.5% confidence level ($F = 6.58$) supporting the inference that the DP atomic heat capacities really are more constant than their modern counterparts.
 27. Fox (Ref. 8) noted of the heat capacities reported in this paper, "So accurate were the results obtained that the Dulong and Petit law could easily have been deduced from them." Because they made no such deduction, Fox inferred that Dulong and Petit were not interested in atomic heat capacities at that time.
 28. Paul Schwarz raised this point during the discussion period following the presentation of this paper in San Diego. Close inspection of the typeface used in the 1819 paper shows that the "r" has 180° rotational symmetry, while the "6" and "9" are related by a 180° rotation about the center of the closed loop.
 29. The statistical analyses reported above, in particular the extent to which specific heat errors for tellurium and cobalt are outliers from the rest of the reported DP specific heats, are unaffected by the choice of the printed 0.0314 or the inferred 0.0335 as the DP specific heat of platinum.
 30. J. J. Berzelius, *Essai sur la théorie des proportions chimiques et sur l'influence chimique de l'électricité*, Méquignon-Marvis, Paris, 1819.
 31. Gates (Ref. 18) deserves credit for bringing this relationship to light. Fox (Ref. 8) points out that Ref. 30 contains atomic weights published a year earlier in Berzelius' *Lärbok i Kemien*. He also notes that Berzelius was in Paris in 1818-19, working in a laboratory with Dulong; this ensures that Dulong and Petit had access to Berzelius' most recent set of weights. Van Spronsen's paper (Ref. 19) prompted me to examine possible sources of DP atomic weights, but his own inspection of those sources was unhelpful, perhaps even misleading. He concentrated on a set of 1815 Berzelian atomic weights, which he rounded. While similar to the 1818 set, they were not identical.
 32. Indeed, they as much as said so: "The reasons which have directed us in our choice [of atomic weights] will be sufficiently explained by what follows." (Ref. 9)
 33. T. Graham, *Elements of Chemistry, with notes and additions by Robert Bridges*, Lea & Blanchard, Philadelphia, PA, 1843.
 34. H. Gates, *Chem. Eng. News*, August 3, 1987, 33.
 35. Australian Broadcasting Corporation, Ockham's Razor 2, ABC Enterprises for Australian Broadcasting Corporation, Sydney, 1988. SCIFRAUD list at LISTSERV.ALBANY.EDU is archived at http://apollo.iwt.uni-bielefeld.de/~ml_robot/Scifraud-archive.html; Macinnis' observations on Dulong and Petit are at http://apollo.iwt.uni-bielefeld.de/~ml_robot/Scifraud-1995/0663.html. Our electronic correspondence began in December 1998.

ABOUT THE AUTHOR

Carmen Giunta is Associate Professor of Chemistry at Le Moyne College, 1419 Salt Springs Rd, Syracuse, NY 13214-1399; giunta@lemoyne.edu. A physical chemist by training, he is particularly interested in applying history of chemistry to chemical education. He maintains the Classic Chemistry web site: <http://webserver.lemoyne.edu/faculty/giunta>