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Revisiting the Pressure-Volume Law in History-What Can it Teach Us About the Emergence of Mathematical Relationships in Science?

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ABSTRACT. In this article the pressure-volume law is reviewed from the point of view of its historical emergence from 1644–1662 and its application in the science classroom. It is contended that mathematical laws in science have value as rich conceptual tools in addition to their role in computation. A classification scheme for algebraic mathematical expressions, based on their historical context, is proposed as a means of assigning significance to the mathematical expressions commonly used in science.

INTRODUCTION

Physical Science courses as taught at the secondary school level have been criticised (Reif 1983) for their reliance on the derivation of mathematical formulae and the use of problems depending on substitution into equations and solution for the unknowns. It has been argued that such courses are dull and boring, have little appeal to female student participation, and do not provide sufficient qualitative background to enrich understanding of the concepts in question. One approach to this dilemma has been the 'concepts before computation' approach (Woolnough and Cameron 1991) which emphasises the meaning of concepts in a qualitative sense before any problems involving mathematical equations are introduced. This approach assumes that mathematical equations have very little to do with scientific concepts and are primarily the means of arriving at solutions to problems. While such an approach does address the need to restrict mindless calculations in science courses, it does not address the conceptual richness that lies behind such mathematical equations as $pv = c$, $E = 1/2\,\mathrm{mv}^2$, $V = IR$, and so on. Another approach to the problem has been to reduce the mathematical component almost to the point where no mathematical equations appear at all. Such an approach obviously has value in the early secondary grades but to teach science at the upper secondary level without any reference to mathematics, the language of science, seems to me to be equivalent to teaching English without learning how to read. In addition to these two approaches there has been a resurgence of interest over the last five years in the use of the history of science in science curricula as a means of solving some of the current dilemmas facing science education. Michael Matthews (1992) argues that incorporating an historical approach in science curricula can "overcome the sea of meaninglessness which has engulfed science classrooms where formulae and equations are recited but few people know what they mean". This article is an attempt to show how a study of the historical background to the pressure-volume law can enhance its meaning and purpose and inform its applications in the science classroom. Such an approach does not involve blind computation but deals with the law and its variations as concepts in themselves. It can be argued, of course, that formulae and equations are simply the means to an end for finding the solution to a problem and it is only necessary to teach students how to drive the equations rather than to understand how they were developed and why they were developed in the first place. After all, in order to drive a motor car one doesn't need to understand how the engine is put together. There is an element of truth in these arguments as any teacher of physical science will appreciate. On the other hand, even though a detailed knowledge of engine construction is not necessary for driving a car, a healthy respect for engine construction is necessary. Regular oil changes and tune-ups are essential for sound motoring. So it is, I would argue, with mathematical equations in science.

The historical approach has been advocated by those who suggest that the history of science, on occasions, anticipates the kinds of alternative frameworks that students bring to the study of science as a result of their past experience (Wandersee 1985). If the historical process is taken far enough, it is believed that the need for conceptual change will be recognized by the student as historical understandings are challenged by new problems – a process which leads ultimately to an adoption of current scientific understandings. It has been suggested that this approach is suitable for the study of concepts like force and motion (Nersessian 1989). Others have argued that such an approach ignores the significant differences that exist between student concepts and those concepts developed by scientists in the early historical period (Gauld 1991). Although it is clear that students have already developed intuitively their ideas about such concepts as pressure and vacuum before formally taught such ideas (de Berg 1992), and that their ideas to some extent (but certainly not completely) may parallel those of the early scientists, this is almost certainly not the case when we consider mathematical equations in science. Such equations are specially constructed concepts and tend not to enter human experience unless especially imposed upon it. This is in contrast to rudimentary ideas developed about motion, pressure, and forces through everyday experience. Thus the historical approach to mathematical ideas is valuable for developing the concept of a mathematical idea in its own right rather than providing reasons for changing a concept. This article is written for upper secondary, lower tertiary teachers of physical science who would like to be able to use mathematical equations not only as computational tools but as rich conceptual tools. By analysing, through an historical study of the pressure-volume law, such questions as, Why use mathematical equations anyway? How easy is it to deduce a mathematical relationship from experimental data? Is it really possible to discover a mathematical law in a school science laboratory? Why express a mathematical relationship in algebraic form?, it is hoped that a more thoughtful approach to the use of mathematical equations in secondary and tertiary science might be the result.

THE PRESSURE-VOLUME LAW IN HISTORY - HOW DID IT EMERGE? A SUMMARY

A broad sketch of the development of the law from Boyle to the current century has been given by de Berg (1990). Here I wish to give a more detailed account of the development of the law from 1644 to 1662 by summarizing the key events examined in some detail by Webster (1966). This summary is designed to inform the process of mathematization in education settings. Certain key historic experiments (the equipment for which is summarized in Figure 1) are closely related to the emergence of the pressure-volume law. In 1644 Torricelli observed that when a tube full of mercury was inverted in a dish of mercury, the mercury in the tube dropped to a height of 29 inches above the level in the dish. While there was much philosophical speculation about the nature of the space above the mercury in the tube, much of the experimentation came to be related to finding the properties of the air that supported such a mercury column. Pascal found that air at the top of a mountain was not able to support as great a height of mercury as at sea level and Roberval inserted a carp bladder into the space above the mercury in a Torricellian-like tube and noticed the great expansion properties of air as the bladder inflated. Air was regarded, therefore, as being related to a spring because of its properties of expansion and compression. Henry Power, in 1653, thought that the elasticity of air may be able to be used to find the height of mountains using Pascal's data and he consequently examined the elastic properties of air using the Torricellian apparatus with different volumes of air above the mercury in the tube to measure the expansion of the air when inverted over a bowl of mercury. No relationship between the elasticity of air and volume of air was able to be found. The invention of the air pump by Von Guericke in 1654 and its improvements by Hooke in 1658 allowed Robert Boyle in 1659 to pump known calculable amounts of air out of an enclosed chamber in which the Torricellian apparatus was placed and to observe to what height the mercury in the tube descended. Experimental difficulties prevented any relationship between the spring of the air, measured by the height of the mercury, and the density of air pushing on the mercury bowl to be found.

In 1661 Power and Towneley admitted known volumes of air above the mercury in the Torricellian apparatus, inverted the tube in a bowl of mercury, noted the height of the mercury above the bowl at the bottom of a hill, repeated the experiment at the top of a hill, and found an inverse proportional relationship between the pressure and volume of the enclosed air. Later in 1661, Robert Boyle departed from using the Torricellian

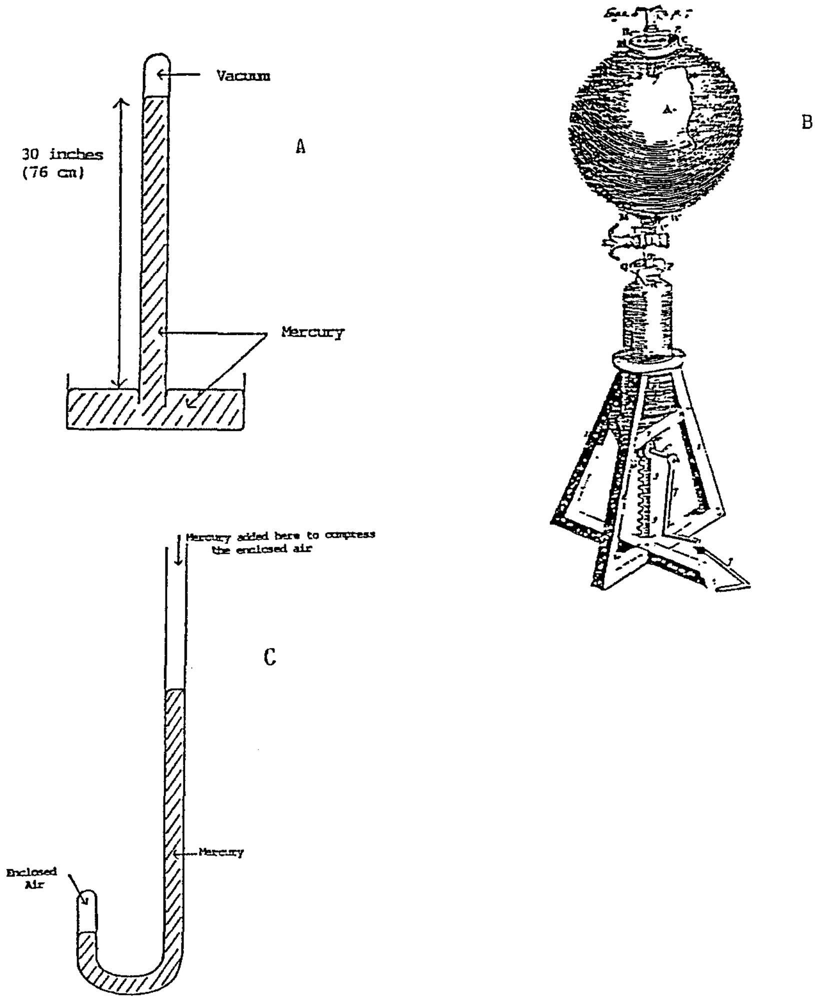


Fig. 1. Historic apparatus used in experiments leading to Boyle's law. A = Torricellian apparatus; B = The pneumatic engine: C = J-tube apparatus for compressing air.

apparatus and used a 'J' tube, closed at one end, open at the other, to compress a volume of air in the closed end by adding increasing amounts of mercury to the open end. Boyle found that the pressure of the enclosed air was directly proportional to its density. Boyle also obtained results, using another piece of apparatus, for the expansion of air and notes, after some correspondence with Towneley, that both his expansion and compression results were consistent with Towneley's earlier proposition for the expansion of air that the pressure (spring) and volume of air were in inverse proportion. A summary of these key events is given in Table I.

TABLE I
Historical events leading to Boyle's law

Experimenter	Year of experiment	Date of publication	Nature of experiment
Henry Power	1653	1663	Measurement of air volumes above mercury before and after inversion using Torricellian apparatus in open air
Robert Boyle	1659	1660	Measured spring of air external to Torricellian apparatus in a pneumatic engine
Henry Power and Richard Towneley	April 1661	1663	Used Torricellian apparatus to measure spring of enclosed air by mercury height above bowl and barometric pressure. Pressure and volume of air in inverse proportion.
Robert Boyle	September 1661	1662	Use of J tube to compress sample of air with mercury. Pressure of air proportional to density of air. Pressure and volume in inverse proportion

Both practical and philosophical considerations motivated the early scientists to try to find a mathematical relationship between the pressure and volume of enclosed air. The operation of water pumps and siphons, the meteorological possibilities of the Torricellian tube, and the possible estimation of the heights of mountains obviously gave impetus to the finding of such a relationship. Speculation about the nature of the space above the mercury in the Torricellian tube and what was responsible for holding mercury to such a height in the tube partly drove Robert Boyle to his 'J' tube experiments to demonstrate that air was capable of supporting even greater heights of mercury than 29 inches. Linus' funicula hypothesis, that the mercury was supported by a rarefied cord of mercury or funiculus, was demolished when Boyle was able to show that air was capable of supporting not only 29 inches but 117 9/16 inches. The phases involved in arriving at the pressure-volume law are now discussed in more detail to attempt to answer the following question.

CAN A MATHEMATICAL RELATIONSHIP EASILY BE DEDUCED FROM EXPERIMENTAL DATA? – THE LESSON OF HISTORY

What is apparent in the historical development of a quantitative law like the pressure-volume law, as discussed by historians such as Webster (1966), is that a development of an understanding of the properties of air in a qualitative sense was absolutely necessary before any law could be established. The notion that air behaved like a spring was an important qualitative link in the chain and how the elasticity of such a spring could be measured formed the next important link in the chain. This proved to be anything but a simple task when early attempts to measure elasticity are examined. In 1653 Henry Power took the Torricellian apparatus and admitted different initial volumes of air on top of the mercury and observed what the new volumes of air were when inverted in a large bowl of mercury. The change in air volume on inversion was taken as a measure of the air's elasticity. No quantitative law between the volume of air and its elasticity could be established because Power did not, at this stage, form a link between the elasticity of air and the pressure of air, found by subtracting the height of mercury above the level in the bowl from the normal barometric height. In 1659 Robert Boyle used his air pump, built by Robert Hooke, to measure the elasticity of the air *external* to the Torricellian apparatus directly by the height of mercury in the Torricellian tube (with no air admitted above the mercury). By pumping out known amounts of air, he tried to establish a relationship between the density of the air and its elasticity measured by the height of the mercury column. It is interesting to note that results for the first two exhaustions of air from the apparatus are consistent with the pressure-volume law as we know it but Boyle, because of experimental difficulties, did not proceed to use these two results to establish a law. This probably reflects the care he believed was necessary in establishing relationships for natural phenomena. A single stroke of the air pump's piston was able to exhaust approximately 5% of the globe's content of air and Boyle found the mercury descend an inch and three-eighths after the first and second suction. If one considers the original air to have 100 density units and an elasticity equivalent to 27 inches of mercury, then pressure/density equals about 0.27 for the original reading and for readings relating to the first two evacuations. Thus, while Boyle appears to have been the first to establish the important link between elasticity and the height of the mercury column above the bowl of mercury, experimental deficiences prevented even a hypothesis being proposed, although the first results indicate a direct proportion between pressure and density of air. It is to Boyle's credit that he recognized how tenuous such a hypothesis would have been given the experimental difficulties he faced.

Power, with Towneley, returned to the problem of the elasticity of air in 1661, and this time, using the Torricellian apparatus as before, measured the elasticity of different trapped volumes of air by comparing the height of mercury above the bowl in the experimental tube with the normal barometric height at altitudes of 800 and 1800 feet. A copy of the results appears in Table II. If one considers the results at 1800 feet for the long tube, then the pressure and volume of air before inversion are 27.4 inches and 50.15 units respectively. Thus $p_1v_1 = 1374$ units. After inversion the volume of enclosed air is 84.75 units and its pressure is 27.4–

TABLE II
Power and Towneley's results for the expansion of air at different pressures. Pressure x. Volume values calculated by the author for comparison with the inverse proportion hypothesis

	Long tube altitude (ft)		Short tube altitude (ft)		
	800	1800	800	800	1800
Volume of enclosed air (0.41 inch units), v_1	50.15	50.15			
Volume of enclosed air (0.84 inch units), v_1			9	9	9
Air pressure (inches), p_1	28.4	27.4	28.4	28.4	27.4
Volume of expanded air (0.41 inch units), v_2	83.8	84.75			
Volume of expanded air (0.84 inch units), v_2			17.58	17.35	17.8
Reduced mercury pressure (inches), p	11.78	11.26	14.2	14.31	13.86
p_1v_1	1424	1374	256	256	247
p_2v_2 $(p_2 = p_1 - p)$	1393	1368	250	244	241

11.26 = 16.14 inches. Thus p_2v_2 = 1368 units. Power and Towneley do not perform calculations like this in their published work. Neither do they state that pressure is inversely proportional to volume although this is inferred in their conclusion (Power 1663, p. 130).

> So that here is now four proportionals, and by any three given, you may strike out the fourth, by Conversion, Transposition, and Division of them. So that by these Analogies you may prognosticate the effects, which follow. in all mercurial experiments, and predemonstrate them, by calculation, before the senses give an Experimental eviction thereof.

The authors emphasize, in the above statement, the importance of using mathematical expressions for making predictions. For any such prediction, of course, the amount of air must be kept constant for this type of experiment and this is an important difference to the experiments of 1653. But, how exactly did the notion of inverse proportion arise? Was it extracted directly from the results or was it initially a proposed hypothesis which proved consistent with the experimental data? Webster (1966, p. 477) suggests that results at different altitudes was probably sufficient to "give them the intuitive realisation of the reciprocal relationship between the pressure and volume of air, although they did not verify this over a wide range of pressures or explore its theoretical significance". Thus a complex interaction between intuition (informed by experiment) and verification through experiment seems to have led to the emergence of the inverse proportion law in this case. Verification over a wider range of pressures was to await the work of Robert Boyle in September of 1661.

Boyle, in 1661, used a 'J' tube, closed at one end and open at the other, to compress a sample of air in the closed end by adding mercury to the open end. The pressure or spring of the air was measured from the difference in mercury heights and the normal barometric height and the density of air was inferred from the height of mercury on the closed-end side of the 'J' tube. The long side of the tube (the open end) was 120 inches long and this required some skill in manufacture to achieve a uniform diameter. Boyle was able to add enough mercury to the open end to double the density of air in the closed end. He observed that when the density of air had been doubled, the pressure acting on the air had been doubled. He (Boyle 1662, p. 156) continues:

> Now that this observation does both very well agree and confirm our hypothesis, will be easily discerned by him that takes notice what we teach; and Monsieur Pascal and our English friend's experiments prove, that the greater the weight is that leans upon the air, the more forcible is its endeavour of dilatation, and consequently its power of resistance (as other springs are stronger when bent by greater weights). For this being considered, it will appear to agree rarely-well with the hypothesis, that as according to it the air in that degree of density and correspondent measure of resistance, to which the weight of the incumbent atmosphere had brought it, was able to counterbalance and resist the pressure of a mercurial cylinder of about 29 inches, as we are taught by the Torricellian experiment; so here the same air being brought to a degree of density about twice as great as that it had before obtains a spring twice as strong as formerly.

Thus Boyle's original statement of the law was as a direct proportion between spring (pressure) and density. Boyle suggests, however, that this result confirmed a hypothesis that the greater the weight that leans upon the air the greater its spring. There is evidence from Boyle's account of the experiment that the hypothesis also included a quantitative estimate of how much the spring would increase if the density was doubled. On doubling the density of the air in the closed end, Boyle (1662, p. 156) recounts, "we cast our eyes upon the longer leg of the glass, on which was likewise pasted a list of paper carefully divided into inches and parts, and we observed, not without delight and satisfaction, that the quicksilver in that longer part of the tube was 29 inches higher than the other". The fact that the 29 inches in the longer tube caused delight and satisfaction suggests that Boyle probably already had the idea that pressure could be proportional to density. We must also remember that his evacuation experiments of 1659, although unable to give a large number of consistent results because of leakage in the globe, had suggested a direct proportion between pressure and density.

After the density doubling experiment Boyle then exhibits a table of results (reproduced in Table III) for a wide range of pressures and volumes for the compression of air, and using different apparatus a table of results for the expansion of air. It appears that Boyle was not certain that expansion of air would follow the same quantitative law as compression of air

TABLE III

Boyle's results for the condensation of air (taken from his 'Defense of Doctrine of Spring of Air . . .', 1662, p. 158)

A table of the condensation of the air

A	A	B	C	D	E
48	12	00	$29\frac{1}{8}$	$29\frac{2}{16}$	$29\frac{2}{16}$
46	$11\frac{1}{2}$	$01\frac{7}{16}$	$29\frac{1}{8}$	$30\frac{9}{16}$	$33\frac{6}{16}$
44	11	$02\frac{11}{16}$	$29\frac{1}{8}$	$31\frac{15}{16}$	$31\frac{12}{16}$
42	$10\frac{1}{2}$	$04\frac{6}{16}$	$29\frac{1}{8}$	$33\frac{3}{16}$	$33\frac{1}{7}$
40	10	$06\frac{3}{16}$	$29\frac{1}{8}$	$35\frac{3}{16}$	35
38	$9\frac{1}{2}$	$07\frac{14}{16}$	$29\frac{1}{8}$	37	$36\frac{15}{16}$
36	9	$10\frac{2}{16}$	$29\frac{1}{8}$	$39\frac{1}{16}$	$38\frac{7}{8}$
34	$8\frac{1}{2}$	$12\frac{8}{16}$	$29\frac{1}{8}$	$41\frac{10}{16}$	$41\frac{2}{17}$
32	8	$15\frac{1}{16}$	$29\frac{1}{8}$	$44\frac{3}{16}$	$43\frac{11}{16}$
30	$7\frac{1}{2}$	$17\frac{15}{16}$	$29\frac{1}{8}$	$47\frac{1}{16}$	$46\frac{2}{5}$
28	7	$21\frac{3}{16}$	$29\frac{1}{8}$	$50\frac{5}{16}$	50
26	$6\frac{1}{2}$	$25\frac{3}{16}$	$29\frac{1}{8}$	$54\frac{5}{16}$	$53\frac{10}{16}$
24	6	$29\frac{11}{16}$	$29\frac{1}{8}$	$58\frac{13}{16}$	$58\frac{2}{8}$
23	$5\frac{3}{4}$	$32\frac{3}{16}$	$29\frac{1}{8}$	$61\frac{5}{16}$	$60\frac{13}{21}$
22	$5\frac{1}{2}$	$34\frac{15}{16}$	$29\frac{1}{8}$	$64\frac{1}{16}$	$63\frac{6}{11}$
21	$5\frac{1}{4}$	$37\frac{15}{16}$	$29\frac{1}{8}$	$67\frac{1}{16}$	$66\frac{4}{7}$
20	5	$41\frac{9}{16}$	$29\frac{1}{8}$	$70\frac{11}{16}$	70
19	$4\frac{3}{4}$	45	$29\frac{1}{8}$	$74\frac{2}{16}$	$73\frac{11}{19}$
18	$4\frac{1}{2}$	$48\frac{12}{16}$	$29\frac{1}{8}$	$77\frac{14}{16}$	$77\frac{2}{7}$
17	$4\frac{1}{4}$	$53\frac{11}{16}$	$29\frac{1}{8}$	$82\frac{12}{16}$	$82\frac{4}{17}$
16	4	$58\frac{2}{16}$	$29\frac{1}{8}$	$87\frac{14}{16}$	$87\frac{3}{8}$
15	$3\frac{3}{4}$	$63\frac{15}{16}$	$29\frac{1}{8}$	$93\frac{1}{16}$	$93\frac{1}{5}$
14	$3\frac{1}{2}$	$71\frac{5}{16}$	$29\frac{1}{8}$	$100\frac{7}{16}$	$99\frac{6}{7}$
13	$3\frac{1}{4}$	$78\frac{11}{16}$	$29\frac{1}{8}$	$107\frac{13}{16}$	$107\frac{7}{16}$
12	3	$88\frac{7}{16}$	$29\frac{1}{8}$	$117\frac{9}{16}$	$116\frac{4}{8}$

AA. The number of equal spaces in the shorter leg, that contained the same parcel of air diversly extended.

B. The height of the mercurial cylinder in the longer leg, that compressed the air into those dimensions.

C. The height of the mercurial cylinder, that counter-balanced the pressure of the atmosphere.

D. The aggregate of the two last columns B and C, exhibiting the pressure sustained by the included air.

E. What that pressure should be according to the hypothesis, that supposes the pressures and expansions to be in reciprocal proportion

and so two different sets of results were submitted. When Towneley reviewed Boyle's expansion results he observed that they followed the same inverse proportion hypothesis that his results of early 1661 had confirmed. Boyle also indicates that his compression results follow the inverse proportion hypothesis. Whether Towneley prompted Boyle to mention this or whether Boyle deduced this on his own account is not as important to us here as the fact that it appears that Boyle used the table of results on compression of air to confirm the inverse proportion hypothesis rather than show that the hypothesis naturally emerges from the data. For example, he describes column E in the table as, "What the pressure should be according to the hypothesis that supposes the pressures and expansions to be in reciprocal proportion".

In summary, then, what can be said about the lesson of history as it relates to obtaining mathematical relationships from experimental data.

1. A rich qualitative understanding of the concepts in question is essential before any quantitative law can be developed.

2. Techniques for measuring scientific concepts need to be perfected before a quantitative law can be established.
3. Quantitative laws rarely emerge from experimental data without prior intuitions as to what the law might look like.
4. Detailed experimental data is more often used to confirm a hypothesis than to abstract a law.
5. The emergence of a quantitative law is a complex process involving intuition and specially contrived experimental procedures.

We are now, I think, in a better position to address the question of the emergence of natural law from experimental data in the context of the science classroom having now briefly observed its emergence in history.

CAN A MATHEMATICAL RELATIONSHIP EASILY BE DEDUCED FROM EXPERIMENTAL DATA? – THE LESSON OF THE SCIENCE CLASSROOM

The lesson of history, previously discussed, attests the fact that even amongst those who are naturally driven to understand the principles of nature, the scientific fraternity, the emergence of a quantitative law is a complex time-consuming process. One must conclude, therefore, that the process must be even more complex in a science classroom. Despite the laudable and grand intentions of the pure discovery method of teaching where "no explicit problem is stated, no procedure is recommended, the pupils simply play with the apparatus and the law is discovered afresh", (Solomon 1980, p. 45), practical and theoretical difficulties, outlined by Solomon (1980, pp. 44–57), mitigate against such a method proving a reality in our science classrooms. We contend here that this is particularly the case for mathematical laws even in their emergence in history as shown in the previous section. What, then, are some of the difficulties teachers face when trying to encourage students to extract a law from quantitative data even in a guided-discovery approach? The difficulties I would like to address are, firstly, those related to how students understand the concept of pressure in a qualitative sense and secondly, how students set about interpreting quantitative data.

As shown previously in the historical analysis, a sound qualitative understanding of pressure (spring) and volume was essential to the eventual emergence of the pressure-volume law. In a study of the responses of 101 students to a problem which asked them to explain why liquid flowing through a burette stops flowing when a bung is inserted at the top, de Berg (1992) found that 74% of the responses involved the concept that enclosed air behaves differently to open air. Twenty-five percent of the responses in this category suggested that when air is enclosed it ceases to exert a pressure. Only one student out of the 101 studied gave a response that represented the scientific view. Thus much more development of a qualitative understanding of 'pressure' is required if the quantitative law is to make any sense, particularly a quantitative law which involves enclosed air.

Now to the situation relating the interpretation of quantitative data. de Berg (1990) relates an experience where students obtained pressure-volume data for a U-tube experiment using water and found, with the teacher's guidance, *PxV* values of 7610, 7596, 7600, 7595, and 7602 units. Because none of these values are *identical* the students could not produce the statement that *PxV* was a constant. This is in contrast to the interpretation given by Power and Towneley to their data of 1661. In Table II, I have calculated what the *PxV* values would have been for their five experiments and it can be seen that no *PxV* values are identical, although they were close enough for Power and Towneley to use an inverse proportional relationship. So, in addition to the complex process of mathematical emergence attested by history, there is the additional problem of interpreting quantitative data in relation to a natural law within the context of the science classroom. To students, a mathematical law is *exact.* All their schooling to this point has reinforced this view. If $PxV = 1000$ units and V is 25 units, then P, by calculation, is exactly 40 units, not 39 or 39.5 units, as might occur with experimental data.

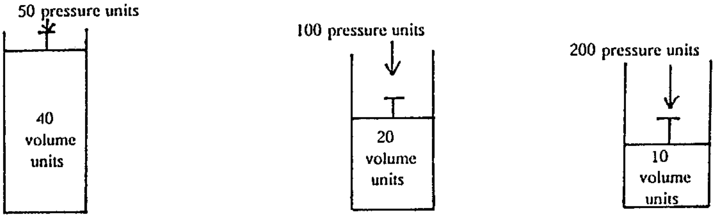
Robert Boyle's understanding of a mathematical description of nature as being an approximation rather than an exact description can be helpful in introducing students to how scientists interpret results which are not exact replicas but nevertheless regarded as supportive of a hypothesis. Boyle (1662, p. 159) comments on his results, recorded in Table III, as follows.

> Now although we deny not, but that in our table some particulars do not so exactly answer to what our formerly mentioned hypothesis might perchance invite the reader to expect; yet the variations are not so considerable, but that they may probably enough be ascribed to some such want of exactness as in such nice experiments is scarce avoidable.

Boyle was tentative enough in his conclusions to also suggest that the hypothesis may not apply for pressures beyond those recorded in his table and that further experimentation would be necessary to decide this question. It cannot be taken for granted that students will automatically interpret quantitative data in the way that a trained eye will interpret it. Access to historical data and its interpretation can be most helpful in preparing students for interpreting the kinds of data they will get in experiments. They can thus be led to interpret their experimental data intelligently rather than believing that most experiments don't work anyway.

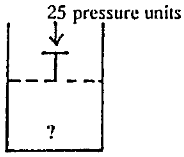
A second illustration I would like to use relates to some research I have been doing with 20 general chemistry students who were given the information shown in Figure 2. From the three results for compression of a gas in a cylinder they had to ascertain what the new values for pressure and volume would be in the four cases shown. Class responses are shown in Table IV. While a high success rate was achieved for (i) and (ii), a very

A student does three experiments with the syringe system as shown below to see what happens when different pressures are put on the plunger. The student finds the following results.



Use these results to help you answer the following questions.

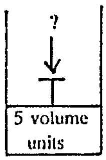
(i) The student exerts 25 pressure units on the plunger as shown



What would the volume of the enclosed air be?

________________ volume units.

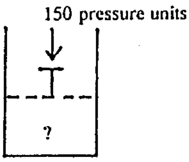
(ii) The student exerts a pressure on the plunger which forms 5 volume units of enclosed air as shown.



What would the pressure on the plunger be?

________________ pressure units.

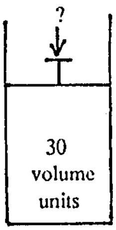
(iii) The student exerts 150 pressure units on the plunger as shown.



What would the volume of the enclosed air be?

________________ volume units.

(iv) The student exerts a pressure on the plunger which forms 30 volume units of enclosed air as shown.



What would the pressure on the plunger be?

________________ pressure units.

Fig. 2. Quantitative exercises relating to air in different states of compression.

TABLE IV
Student ($n = 20$) responses to the exercise shown in Figure 2

Exercise part	Correct answer	Number of students with correct answer	Number of students with '15' for part (iii)	Number of students with '75' for part (iv)
(i)	80	19		
(ii)	400	19		
(iii)	13.3	2	18	
(iv)	66.6	2		17

low success rate was achieved for (iii) and (iv). What is startling is that while the inverse proportion hypothesis was used to get the answers for (i) and (ii), the majority of students used an arithmetic averaging principle to arrive at 15 and 75 units instead of 13.3 and 66.6 respectively for parts (iii) and (iv). They observed that 150 pressure units was the average of 100 and 200 pressure units, so the volume must have been the average of 10 and 20 volume units, that is, 15 units. Thirty volume units was observed to be the average of 40 and 20 units so the pressure was regarded to be the average of 50 and 100 units, that is, 75 units. This illustrates how easy it can be to misinterpret quantitative data if the physical principle or law upon which a system is operating is ignored. So, while algorithmic substitution of data into a formula can become a meaningless exercise, it can be an essential exercise if correct predictions are to be made from experimental results, and this need not be meaningless if the rich conceptual background to the formula is appreciated. Most of the mathematical formulae used in modern physical science courses appear in algebraic form and we will now examine the purposes for using formulae in this format.

WHY IS THERE A NEED TO WRITE NATURAL LAWS IN ALGEBRAIC FORMAT?

Previous data on this topic (de Berg 1990) shows that the pressure-volume law was originally expressed in words, that is, in verbal format. By the middle of the nineteenth century with the development of thermodynamics, William Thomson (Lord Kelvin) was using the pressure-volume law in algebraic format, $pv = c$. The historical data dealt with earlier shows us that the algebraic format of a law is not necessary for making predictions. This is certainly the case with the way Power and Towneley treated their results, and from the student exercise set in Figure 2, although it is clear that predictions can be made from a mathematical statement in algebraic format.

To understand the significance of expressing a mathematical relationship, such as the pressure-volume law, in algebraic format one has to revisit the development of thermodynamics in the 1840's and 1850's particularly. Because of the need to improve the efficiency of air and steam engines an explosion of theoretical development occurred in relation to the properties of gases. I will deal here with just one of the lines of theoretical development, that of the difference in heat capacity of a gas at constant pressure and at constant volume, to illustrate this point. From, $pv = c$, and applying the laws of calculus, Thomson rewrites this expression in the form, $\mathrm{d}p/\mathrm{d}v = -p/v$. Using this expression and the following two theorems derived from Carnot's theory of heat,

1. $M\,\mathrm{d}v + N\,\mathrm{d}t = K\,\mathrm{d}t$ where
   M = heat absorbed at constant temperature
   N = heat absorbed at constant volume
   K = heat absorbed at constant pressure
2. $\mathrm{d}p/\mathrm{d}t = \mu M$, where μ is Carnot's function,

Thomson (1851, pp. 200–205) derives the following expressions.

From (1) $\rightarrow K - N = M\,\mathrm{d}v/\mathrm{d}t$

$$M = \mathrm{d}t/\mathrm{d}v\ (K - N)$$

$$M = (-\mathrm{d}p/\mathrm{d}v)/(\mathrm{d}p/\mathrm{d}t).\ (K - N), \text{ using}$$
$$\mathrm{d}p = (\partial p/\partial v)\,\mathrm{d}v + (\partial p/\partial t)\,\mathrm{d}t = 0\,,$$

although Thomson doesn't use partial derivative symbols.

Therefore, $(K - N) = -M(\mathrm{d}p/\mathrm{d}t)/(\mathrm{d}p/\mathrm{d}v)$.
Using (2) $\rightarrow$, $(K - N) = (\mathrm{d}p/\mathrm{d}t)^2/(\mu. - \mathrm{d}p/\mathrm{d}v)$.

Now, using, $\mathrm{d}p/\mathrm{d}v = -p/v$, and a corresponding expression for $\mathrm{d}p/\mathrm{d}t$, Thomson arrives at the expression,

$$K - N = E^2pv/[\mu(1 + Et)^2],$$

where E is the expansion coefficient for a gas, 1/273. It can be shown that for one mole of gas, this expression is equivalent to the modern gas constant, $R = 8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$. Thus the heat capacity of a gas differs according to whether heat is supplied at constant pressure or at constant volume, and for normal conditions the difference is constant and independent of the identity of the gas.

The point of the previous exercise is to demonstrate that algebraic expressions are primarily useful for theoretical development which leads not only to new data but new concepts. This development takes place through the laws of mathematics. Despite this, a significant number of students still see the major role of mathematical algebraic expressions as that of prediction rather than for theoretical conceptual development. See Figure 3

A large portion of the mathematical component of modern physical science courses consists of algebraic expressions and it is vitally important for students to appreciate them as important expressions of scientific concepts rather than mystical tools for problem-solving if blind substitution procedures are to be avoided. One approach to this problem is to classify

TABLE V
Classification of algebraic expressions relating to Boyle's law. (p = pressure; v = volume; c = constant; d = density; m = mass; n = moles; M = molar mass)

Algebraic expression	Definition-based	Empiric-based	Mathematic-based
$pv = c$		√	
$\frac{dp}{dv} = \frac{-p}{v}$			√
$d = \frac{m}{v}$	√	√	
$n = \frac{m}{M}$	√		

Question 1. As far as I know, when Boyle published his law in 1662.
a) He stated his law using algebraic symbols such as $P \propto 1/V$,
b) He stated his law by plotting pressure against volume,
c) He stated his law in words,
d) All of the above.

Question 2. It is said that stating a law using algebraic symbols such as, $P_1V_1 = P_2V_2$, has advantages over stating the law in words. This advantage relates primarily to the fact that,
a) It is possible to generate new expressions using the laws of mathematics,
b) Symbols take up less room than words,
c) It is more mathematically correct to use symbols rather than words.
d) It is possible to predict, for example, what pressure would be needed to give rise to any suggested volume.

Frequency of responses for Questions 1 and 2 for a total of 35 students.

	(a)	(b)	(c)	(d)
Question 1	0	5	3	27
Question 2	15	7	2	11

Fig. 3. Student responses to two multiple-choice questions relating to mathematization in science.

algebraic mathematical expressions according to their *origin* which ultimately involves their history.

(i) *Empiric-Based Expressions*

These are the algebraic expressions that are based upon experimental data. For example, $pv = c$, is based upon the data of Boyle, Power and Towneley and could be classified as empiric-based. It doesn't mean that the equation was necessarily abstracted from the data, but as has been shown, is often confirmed by the data. However, whether abstracted or confirmed, it would be empiric-based.

(ii) *Mathematic-Based Expressions*

These are the algebraic expressions derived from other algebraic expressions using the laws of mathematics. For example, $dp/dv = -p/v$, derived from, $pv = c$, by the rules of calculus would be a mathematic-based expression as is the expression for $K - N$ derived previously. The fact that an algebraic expression is classified as mathematic-based according to origin does not preclude its later empirical justification. It also follows that classifying an algebraic expression as empiric-based according to origin does not preclude its later derivation mathematically within a theoretical model such as the kinetic theory. This is in fact the case for, $pv = c$. The strong link between theory and experiment has undoubtedly been one of the features of modern science responsible for its success.

(iii) *Definition-Based Expressions*

The value of the constant in the equation, $pv = c$, changes as the amount of gas being studied changes. A look at the 'pv' values in Table II for Power and Towneley's results will confirm this. During the middle of the nineteenth century the notion of a standard amount of substance became important in comparing properties of gases and in 1865 A. W. Hoffman chose one litre of hydrogen at 0 °C and 760 mmHg pressure as the standard. By international agreement in 1897 the standard was chosen as 22.4 litres of oxygen at 0 °C and 760 mm Hg pressure. In 1961, also by international agreement, the standard was changed to 12 g of the carbon isotope, ^{12}C. This standard represents one mole of a substance. The use of the definition for number of moles of gas as mass divided by molar mass based on the ^{12}C isotope, $n = m/M$, is thus definition-based. The expression for amount of substance could have been defined in other ways. This is characteristic of definition-based expressions.

It would appear that some algebraic expressions do not fall precisely into only one of these three categories just discussed. For example, the formula for density as mass per unit volume, $d = m/v$, reflects both empirically determined fact, that is, the uniform composition of pure homogeneous substances, and the definition of m/v as density. Such expressions could be classified as empiric-definition-based. This is reflected in Table V by the presence of a tick in the empiric and definition columns. Paul Gardiner (1975, pp. 18–19) discusses the difficulty of exclusively categorizing certain mathematical statements when he discusses the differences between definition statements and law statements. He observes that for some expressions the distinction is not as simple and sharp as one might think because "some definition statements hide within them certain law-like assumptions about nature". This would appear to be the case for density.

CONCLUSION

The historical and pedagogical analysis of the pressure-volume law discussed in this article has value for the classroom practitioner in the following areas.

1. Qualitative understandings of the concepts in the mathematical description of a natural law need to be enriched before the mathematical description itself makes sense. Some of the early experimenters with air believed that once one isolated or enclosed a body of air it ceased to exert a pressure because it was no longer acted upon by the ocean of air above it. Students, while not necessarily thinking of pressure in this way, also believe that enclosed air ceases to exert a pressure.
2. More often than not, experiments tend to be contrived in order to test an hypothesis rather than to discover an hypothesis. This does not preclude, however, the role of experience and experiment in hypothesis generation or those rare moments in the history of science when it may be said something was 'discovered'. Abstracting a law from a set of data can prove to be a difficult and tricky business particularly when the numbers suggest an arithmetic averaging operation whereas an inverse proportion principle applies.
3. The history of the pressure-volume law is most instructive from the point of view of what kinds of data are regarded as significant in relation to an hypothesis. Students regard mathematical laws as exact and exposure to Power and Towneley's or Boyle's data can be helpful in learning under what circumstances scientists regard experimental data as supporting an hypothesis.
4. Algebraic mathematical laws are important in theory generation. A classification scheme based on the origin of these laws can be helpful in reminding the students that they are dealing with rich conceptual tools rather than just magic wands that pop out answers to problems.

The use of mathematical formulae in science can thus be far more significant than just algorithmic substitution and solution, although there is a place for such procedures. There is a rich history behind the origin of many formulae used in science and reference to this history and the usefulness of different mathematical formats may help the student appreciate the complexity of the relationship between theory and experiment and give a sense of clarity, purpose and direction which is unattainable with simple substitution procedures. The use of a classification scheme for algebraic expressions, like that discussed in this article, gives students the opportunity to think more about the significance of the mathematics they are using, particularly when limitations on time and space preclude a detailed historical profile for every mathematical formula. Such a classification scheme assists the teacher in answering simple but provocative questions such as, "But sir, why is, $pv = c$, and not, $p/v = c$?" Reference to historical issues related to mathematical formulae will obviously depend on the level of science taught. The approach advocated here may be more suitable for those pursuing an academic science career rather than a vocational career such as nursing. Such issues have yet to be addressed. What is clear is that many mathematical expressions used in science have a function far beyond that of problem-solving tools but have, in fact, constituted part of the fabric of science itself. It is a healthy respect for this fact which I think is worth communicating in our science courses.

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