

The historical development of the pressure-volume law for gases

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Dr Kevin de Berg has taught science and mathematics in secondary schools and currently teaches tertiary level chemistry and science education. He has recently spent six months in England working with Professor David Waddington's Science Education Group at the University of York. The subject of this paper represents part of the research recently completed for a masters degree at Curtin University.

ABSTRACT

The common approach taken to the teaching of the quantified aspects of science in our classrooms has received recent criticism from philosophers of science and education. The nature of the quantified forms in science is addressed in this paper by outlining the development of an historical profile for the pressure-volume law for gases.

INTRODUCTION: A LABORATORY EXPERIENCE

On one occasion whilst teaching the gas laws to a group of sixteen year-olds, I decided to introduce Boyle's law, not by simply writing $P \propto 1/V$ on the board and then proceeding with some calculations using $P_1 V_1 = P_2 V_2$, but by having the students take pressure and volume measurements for air in a U-tube system and arrive at Boyle's law through a

process of guided-discovery. On this occasion I suggested that the students evaluate P/V and PV for each pressure and volume measurement and see if this might help in establishing a relationship between P and V. A typical set of student results is shown in Table 1. I was extremely pleased that every student was getting effectively a constant value for the PV column but certainly not for the P/V column and of course expected Boyle's Law to emerge from the data with ease.

However, when I asked the students to examine their results and try to come to some conclusion about a relationship between P and V, all of them (and they were a bright class by traditional standards) looked absolutely mystified at me. No one suggested PV was constant and here I was trying to cajole them into seeing, in my terms, that we had deduced a relationship. I felt discouraged, bewildered and annoyed that this group of

TABLE 1
Pressure (P) and volume (V) data obtained with a
U-tube system for a fixed amount of air

V(cm)	P(mm Hg)	PV	P/V
10	761	7610	76.1
9	844	7596	93.8
8	950	7600	118.8
7	1085	7595	155.0
6	1267	7602	211.0

intelligent students could not 'see' Boyle's law in their results and concluded that this occasion was their very first exposure to the dynamic emergence of quantification in science.

Reflecting on this situation, I realized that my students up to this point in time had been denied access to one of the most important aspects of our cultural heritage. They had no difficulties performing calculations with the gas equations, as I later discovered, but they had no understanding of how and why the equations were developed or the part they have played in our cultural and technological development. Stenhouse argues that

What is inculcated in a great deal of science education is, all too often, not understanding, but rather a sort of recipe book acquaintance with a number of mathematical techniques which tend often to be used on an ad hoc basis without any proper understanding either of the mathematical theory and assumptions on which the techniques are based, or of the subject matter to which they are applied. (Stenhouse, 1985, p.21)

My students, in fact, were quite justified in looking mystified at my conclusion that PV was constant if they understood the term 'constant' to mean 'identical'. There are no identical PV values in Table 1. However, the process of examining real data obtained experimentally and deducing corresponding relationships is a very significant part of the scientific enterprise. In this paper the dynamic emergence of the pressure-volume law for gases is addressed through an examination of the historical development of the law. A dynamic emergence reveals a pattern of concept development that addresses the evolution of a concept, the interrelationship of the separate parts of a concept, and its background and significance.

THE PRESSURE-VOLUME RELATIONSHIP FOR GASES

An historical study of primary source documents relating to the pressure-volume law was undertaken in 1986 at the British Museum and Library in London. The historical profile thus

constructed is shown in Table 2. Some of the occurrences listed in this table may not represent the very first historically, although an attempt has been made to locate the origins of the various forms of the law from significant historical documents. Further detailed historical investigation may shed further light on the emergence of some of these quantitative forms.

The work of Boyle

Robert Boyle (1627-1691) was the first to publish results for the expansion and contraction of air which demonstrated an inverse proportional relationship (see Table 3), although this relationship had been suggested by other workers such as Townley, Hooke and Brouncker. The data were obtained, using apparatus similar to that shown in Figure 1, to refute the Funicular hypothesis that mercury in a narrow tube inverted in a bowl of mercury (Figure 2) remained suspended at a height of 30 inches above that in the bowl because of its attraction to a very fine substance, called Funiculus, capable of forcible distension. Boyle was able to show experimentally through the use of a U-tube closed at one end and open at the other (Figure 1) that air could support not only 30 inches of mercury but a much greater height than this, in fact 117 9/16

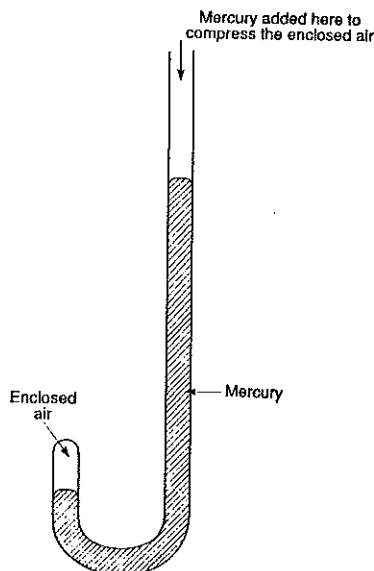


FIGURE 1: The U-tube system used for studying the condensation and rarefaction of air.

TABLE 2
Historical profile of the pressure-volume law

Year	Form	Context	Reference
1662	Pressures and expansions in reciprocal proportions; Boyle, Townley, Hooke, Brouncker.	Data to refute Funicular hypothesis	Boyle (1662, pp.156-163)
1676	Air is condensed in proportion to the weight with which it is loaded; Mariotte	In answer to 'question one may ask'	Mariotte (1676, pp.88-92)
1768	Proportional symbol, α , introduced; Emerson	Mathematical notation	Emerson (1768, p.297)
1849	p_v is constant - Law of Mariotte and Boyle; W. Thomson	Thermodynamic study of steam and air engine.	Thomson* (1882, p.131)
1849	$\frac{dp}{dv} = -\frac{p}{v}$ - Boyle and Mariotte's Law; W Thomson	Thermodynamic study of steam and air engine.	Thomson* (1882, p.204)
1851	$pu = p^1u^1$; W. Thomson	Thermodynamic study of steam and air engine.	Thomson* (1882, p.219)
1902	$p v = c$; $p_1 v_1 = p_2 v_2$; W. Ostwald	Pedagogic - textbook	Ostwald* (1902, p.76)
1953	$v \propto 1/p$; W.G. Henderson	Pedagogic - textbook	Henderson (1953, p. 158)

Note: These references (*) were consulted at the British Museum and Library

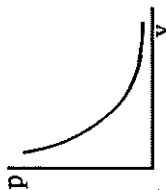


TABLE 3

Boyle's results for the condensation of air (Taken from his 'Defence 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		$29\frac{7}{8}$	$29\frac{7}{8}$
46	$11\frac{1}{2}$	$01\frac{7}{8}$		$30\frac{9}{16}$	$33\frac{1}{8}$
44	11	$02\frac{1}{4}$		$31\frac{1}{2}$	$31\frac{1}{2}$
42	$10\frac{1}{2}$	$04\frac{1}{4}$		$33\frac{1}{8}$	$33\frac{1}{2}$
40	10	$06\frac{1}{2}$		$35\frac{1}{4}$	35
38	$9\frac{1}{2}$	$07\frac{1}{2}$		37	$36\frac{1}{4}$
36	9	$10\frac{1}{2}$		$39\frac{1}{8}$	$38\frac{1}{4}$
34	$8\frac{1}{2}$	$12\frac{1}{4}$		$41\frac{1}{8}$	$41\frac{1}{4}$
32	8	$15\frac{1}{8}$		$44\frac{1}{8}$	$43\frac{1}{4}$
30	$7\frac{1}{2}$	$17\frac{1}{4}$		$47\frac{1}{8}$	$46\frac{1}{4}$
28	7	$21\frac{1}{8}$		$50\frac{1}{4}$	50
26	$6\frac{1}{2}$	$25\frac{1}{4}$		$54\frac{1}{4}$	$53\frac{1}{4}$
24	6	$29\frac{1}{2}$		$58\frac{1}{4}$	$58\frac{1}{4}$
23	$5\frac{1}{2}$	$32\frac{1}{4}$	Added to $22\frac{1}{2}$ makes	$61\frac{1}{4}$	$60\frac{1}{4}$
22	$5\frac{1}{4}$	$34\frac{1}{4}$		$64\frac{1}{4}$	$63\frac{1}{4}$
21	$5\frac{1}{8}$	$37\frac{1}{4}$		$67\frac{1}{4}$	$66\frac{1}{4}$
20	5	$41\frac{1}{4}$		$70\frac{1}{4}$	70
19	$4\frac{1}{2}$	45		$74\frac{1}{4}$	$73\frac{1}{4}$
18	$4\frac{1}{4}$	$48\frac{1}{4}$		$77\frac{1}{4}$	$77\frac{1}{4}$
17	$4\frac{1}{8}$	$53\frac{1}{4}$		$82\frac{1}{4}$	$82\frac{1}{4}$
16	4	$58\frac{1}{4}$		$87\frac{1}{4}$	$87\frac{1}{4}$
15	$3\frac{1}{2}$	$63\frac{1}{4}$		$93\frac{1}{4}$	$93\frac{1}{4}$
14	$3\frac{1}{4}$	$71\frac{1}{4}$		$100\frac{1}{4}$	$99\frac{1}{4}$
13	$3\frac{1}{8}$	$78\frac{1}{4}$		$107\frac{1}{4}$	$107\frac{1}{4}$
12	3	$88\frac{1}{4}$		$117\frac{1}{4}$	$116\frac{1}{4}$

A.A. 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 counterbalanced 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.

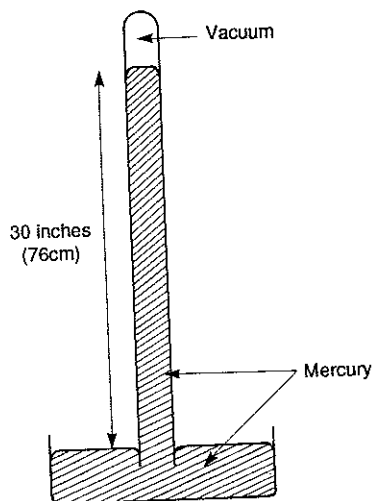


FIGURE 2: Torricellian apparatus

Note: The figure in column C should read $29\frac{2}{16}$

inches of mercury according to the results in Table 3. The experiments involved trapping air in the closed side of the U-tube with mercury and then compressing the air in the closed side by adding additional mercury to the open side. Since Funiculus was not able to pull up a column of mercury to a height greater than 30 inches, it could not be responsible for attracting mercury to a height of $117\frac{9}{16}$ inches (Boyle, 1662, p.159). Thus Boyle was able to dispense with the Funicular hypothesis.

It is clear that the U-tube experiments giving rise to the inverse proportional relationship between pressure and volume for air were designed specifically to refute Linus' Funicular hypothesis; the mathematical relationship between pressure

and volume giving weight to the exactness of Boyle's measurements and thus his hypothesis that it was the external air pressure which was responsible for supporting the 30 inches of mercury in the Torricellian experiment (Figure 2). In general, however, Boyle indicates that his experiments "touching the nature of the air would not be useless to the world" and "would be grateful to the lovers of free and real learning". Boyle (1660, p.6) continues, "that the air being so necessary to human life...any considerable discovery of its nature seems likely to prove of moment to mankind...any experiment that is new concerning a thing,... may not only prove of some advantage to human life, but gratify philosophers, by promoting their speculations on a subject." Also, there is evidence from Boyle's account of

his experiments that he considered that the proposed reciprocal proportion hypothesis might only be an approximation. He says,

the proportion was suitable enough to what might be expected to allow us to make this reflection upon the whole; that whether or no the intimated theory will hold exactly (for about that, as I said before, I dare determine nothing resolutely till I have further considered the matter). (Boyle, 1662, p.162)

The work of Mariotte

The pressure-volume relationship for air is said (Magie, 1935) to have been independently discovered on the European Continent in 1676 by Edme Mariotte (1620-1684). Mariotte, unlike Boyle, does not provide a table of results for pressure-volume measurements. He does, however, quote the results of a number of experiments performed with the Torricellian apparatus (Figure 2) and a U-tube (Figure 1). Knowing from qualitative experiments that air has weight and spring, Mariotte commenced his quantitative study by testing a hypothesis. The hypothesis reads (Mariotte, 1676, p.88), "The first question that we can ask is to know if the air condenses itself precisely in the proportion of the weights with which it is loaded, or if this condensation follows other laws and other proportions". On the basis of air being condensed in proportion to the weight with which it is loaded, Mariotte predicts what 12 1/2 inches of mercury in a straight glass tube should become when inverted in a mercury dish. The prediction (25 inches of air on top of 14 inches of mercury) is tested by experiment and Mariotte concludes (1676, p.90) "I was not deceived in my expectations". Thus he was able to propose that (1676, p.91), "air is condensed in proportion to the weight with which it is loaded". The pressure-volume relationship for a gas has often been referred to as the law of Boyle and Mariotte although the latter's contribution is regarded by some (Mykie, 1965, p.13) as inferior to that of Boyle's in quality. As well as differences in quality of work there is a difference in the contexts in which the law emerges. Whilst the context in Boyle's case is the refutation of another's hypothesis, the context in Mariotte's case is simply "a question that we can

ask". In one case (Boyle) the context is extrinsic and in the other case (Mariotte) intrinsic.

Expressing relationships

In Boyle's and Mariotte's works the pressure-volume relationship is never stated in algebraic symbols. It is only stated verbally in such phrases as (Boyle, 162, p.158), "pressures and expansions in reciprocal proportion", and (Mariotte, 1676, p.91), "air is condensed in proportion to the weight with which it is loaded". In fact, up to the time of Descartes (1596-1650), and some time after, quantitative relationships were written predominantly in words or in word abbreviations. Flegg (1983) notes that while our modern algebraic notation for quantitative relationships came with Descartes in the seventeenth century, it was not immediately popular with his mathematical contemporaries. By the eighteenth century however the new notation had become the norm for mathematicians throughout Western Europe. Flegg, in reflecting on the reasons for the late adoption of abstract symbols in mathematics, makes the following pertinent comment:

Mathematical ideas were explained in words; mathematical arguments were written in words. To adopt abbreviations of words is therefore a natural step; the change to abstract symbolism demands an intellectual leap of extraordinary magnitude. (1983, p.224)

This leap of extraordinary magnitude is witnessed in the forms in which the pressure-volume law has been expressed historically. Although algebraic forms of the pressure-volume law for gases appear as early as in the work of Bernouille (1738) and Waterston (1892), these forms make use of symbols relating to the peculiar model of a gas relating to kinetic theory that is proposed in each case and are not, therefore, included in Table 2. In Table 2, the general algebraic forms of the pressure-volume law used by Lord Kelvin (William Thomson) as early as 1849 are included. The context in each case in which the shown algebraic forms appear is a theoretical, thermodynamic study of the steam and air engines. This study makes extensive use of calculus as shown in the derivative form of the pressure-volume law.

A graphical interpretation of the inverse proportion was only made possible after Descartes's introduction of coordinate geometry. Although Waterston (1892, p.275) uses a pressure-volume graph as early as 1845, a more extensive background discussion of the graphical relationship is given by Wilhelm Ostwald in his *Principles of inorganic chemistry* published in 1902. Ostwald explains the usefulness of the graphical technique in the words:

In many cases, however, especially in the investigation of new relations, an algebraic expression for a really existing dependence is not known. In such cases it is important to possess a method which allows of showing clearly the connection between the magnitudes, so that the general relations can be judged. For this purpose the representation by means of coordinates is generally used in the experimental sciences. (Ostwald, 1902, p.73)

The proportional symbol, $\propto$, whilst introduced by Emerson in 1768 (Cajori, 1974, p.297) does not appear to be used in the pressure-volume law until this century.

CONCLUSION

The historical profile of the development of the pressure-volume law for gases reveals that the emergence of the law is dynamic in that the forces operating which lead to the expression of a quantified form are revealed and this revelation occurs in a time context. This is important in assessing textbook statements of the pressure-volume law such as the following :

Robert Boyle carried out this experiment as early as 1660 and discovered that if he plotted a graph of the reciprocal of the volume of the enclosed gas against the total pressure acting on the gas (which is equal to the applied pressure plus the pressure due to the atmosphere), he obtained a straight line graph through the origin. From this he concluded that $P \propto 1/V$ (T constant). (Parham & Webber, 1984, pp.114-115)

If one compares this statement with the profile constructed in Table 1 from primary sources, it

becomes obvious that a grossly distorted picture of Boyle's Law is being portrayed in the textbook statement. Nowhere in Boyle's publication is pressure plotted against the reciprocal of volume. The dynamic development of science is forgotten if only summary historical statements are connected to the discovery of important scientific laws.

How can the teaching of the pressure-volume law become more dynamic? It would appear that the place to start might be with semi-quantitative exercises which involve the manipulation of the variables used in the quantified forms. A discussion of common occurrences such as the drinking of fruit juice from a popper container in terms of the pressure and volume changes of air could be the substance of such exercises. Experience in handling these problems gives students an understanding of what is meant by the pressure and volume of air before such variables are treated in an algebraic sense. Students find it difficult, for example, to think of the enclosed air in the U-tube apparatus related in the introduction to this paper as exerting a pressure. The semi-quantitative exercises envisaged would help to solve such a difficulty. Both Boyle and Mariotte had developed the concepts of 'weight' and 'spring' from qualitative experiments with air before the inverse proportion law was proposed. A forthcoming paper will deal with specific examples of semi-quantitative exercises dealing with the pressure and volume of air which could be used as an introduction to work on the pressure-volume law.

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ROY W STANHOPE AM

Those attending CONASTA year by year or only attending periodically will have met Roy who has attended and actively participated in 35 of the 37 conferences - he was overseas in 1968 and 1974. As editor, I house the archival issues of *ASTJ*. An examination of the past issues sees Roy's name appearing in the first issue and many more. He was a founding member of ASTA and had a significant influence on the introduction of this journal. We sometimes forget our own history and until recently Australia as a whole paid little attention to events gone by. The Bicentennial gave Australian science teachers the opportunity to reflect on the history of science and of science education in Australia through the special 1988 issue. Roy's contribution was evident in his review of ASTA and the State and Territory Associations. The annual presentation at CONASTA which addresses a current scientific topic is named in his honour; Roy delivered the first of these in Perth in 1966.



These contributions, and many more relating to his distinguished teaching career, resulted in Roy being awarded a Member of the General Division of the Order of Australia in 1989.