

Ask the Historian

The Universal Gas Constant R

by William B. Jensen

Question

Why is the universal gas constant in $PV = nRT$ represented by the letter R ?

Donald R. Paulson
Department of Chemistry
California State University
Los Angeles, CA 90032

Answer

This is best answered by tracing the origins of the ideal gas law itself. One of the first persons to combine Boyle's law (1662) relating volume and pressure and Gay-Lussac's law (1802) relating volume and temperature in a single equation appears to have been the French engineer, Benoit-Pierre-Émile Clapeyron (1799–1864). In his famous memoir of 1834 on Carnot cycles, he wrote the combined equation as:

$$pv = R(267 + t) \quad (1)$$

where t is the temperature in degrees centigrade (1). In 1850, the German physicist, Rudolf Clausius (1822–1888), using the experimental data of the French chemist, Henri Victor Regnault (1810–1878), reevaluated the constant inside the parentheses and rewrote the equation (2) as:

$$pv = R(273 + t) \quad (2)$$

and in 1864 he further simplified it (3) by substituting the absolute temperature T in place of the $(273 + t)$ term:

$$pv = RT \quad (3)$$

Being French, Clapeyron had attributed the volume-pressure law to the French scientist, Edmé Mariotte (1620–1684), rather than to Robert Boyle, and Clausius did not question this choice. Indeed, he explicitly proposed that the combined equation be called the Mariotte–Gay-Lussac law or the M–G law for short.

Both Clapeyron and Clausius had used the volume per unit mass of gas rather than the volume per mole of gas in their equations. This meant that their gas constant R was not universal for all gases but was rather a specific constant whose value varied from one gas to another and was, as Clausius noted, roughly inversely proportional to the density of the gas in question. In other words, just as the volume per unit mass and the volume per mole are related by the equation:

$$v = V/m = (V/n)(n/m) = (V/n)(1/M) \quad (4)$$

where $M = m/n$ is mass per mole or the molecular weight, so the universal gas constant R and the Clapeyron-Clausius' specific gas constant (designated here as R' to avoid confusion) are related by the equation:

$$R' = R/m = (R/n)(n/m) \\ = \text{constant}/M = \text{constant}'/\text{density} \quad (5)$$

where by Avogadro's hypothesis the molecular weight of a gas at constant PVT is directly proportional to its density (4).

The first person to convert the specific constant of Clapeyron and Clausius into a universal gas constant appears to have been Clausius' student, the German chemist, August F. Horstmann (1842–1929), who in 1873 rewrote equation 3 as:

$$up = RT \quad (6)$$

where p and T have their earlier meaning but u is "the volume of a molecular weight [i. e., mole] of the gas" and " R is the constant for the G–M law with regard to the molecular [in other words, molar] volume" (5).

So why did Clapeyron choose the letter R for the constant in his gas law? The fact is that he doesn't explicitly tell us why and we are left with two speculative answers: (a) it was arbitrary; or (b) it stood for *ratio* or one of its French equivalents: *raison* or *rapport*, since Clapeyron noted that the value of R for each gas was obtained by evaluating the constancy of the ratio $pv/(267 + t)$ over a range of pressures and temperatures, a point also emphasized by Clausius using the revised ratio $pv/(273 + t)$.

Given IUPAC's penchant for naming constants after famous scientists, this suggests that it might not be inappropriate to name R in honor of Regnault whose accurate experimental data were used by Clausius not only to correct the conversion factor between the centigrade and absolute temperature scales but also to evaluate the values of R using the above ratio (6). It is also interesting to note that Clausius was aware that Regnault's data clearly showed that (2):

...the more distant, as regards pressure and temperature, a gas is from its point of condensation the more correct will be the law [i. e. the more constant R]. Whilst its accuracy, therefore, for permanent gases in their common state is so great, that in most investigations it may be regarded as perfect, for every gas a limit may be imagined, up to which the law is also perfectly true; and in the following pages, where permanent gases are treated as such, we shall assume the existence of this ideal condition.

In 1864 Clausius further introduced the term "ideal gas" to describe gas behavior under these limiting conditions (7).

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Literature Cited

1. Clapeyron, E. Mémoire sur la puissance motrice de la chaleur. *J. l'école polytechnique* 1834, 14, 153–190. An English translation appears in Mendoza, E., Ed., *Reflections on the Motive Power of Fire and Other Papers on the Second Law of Thermodynamics*; Dover: New York, NY, 1960; pp 71–105.
2. Clausius, R. Über die bewegende Kraft der Wärme, und die Gesetze, welche sich daraus für die Wärmelehre selbst ableiten lassen. *Ann. Phys.* 1850, 79, 368–397, 500–524. This memoir has been translated into English and reprinted many times, including: (a) Clausius, R. On the Moving Force of Heat and the Laws of Heat which may be Deduced Therefrom. *Phil. Mag.* 1851, 2, 1–21, 102–119; (b) Clausius, R. *The Mechanical Theory of Heat*; Van Voorst: London, 1867, pp 14–80; (c) Magie, W. F., Ed., *The Second Law of Thermodynamics*; Harper: New York, 1899; pp 63–108; (d) Mendoza, E., Ed., *Reflections on the Motive Power of Fire and Other Papers on the Second Law of Thermodynamics*; Dover: New York, NY, 1960; pp 107–152.
3. Reference 2b, p 259.
4. The practice of writing R as a specific constant persisted in the physics literature well into the 20th century. See Kennard, E. H. *Kinetic Theory of Gases*; Macmillan: New York, 1938; pp 23, 26.
5. Horstmann, A. F. Theorie der Dissociation. *Ann. Chem.* 1873, 170, 192–210.
6. Though explicitly discussing his work, Clausius fails to give specific references for Regnault. However, the papers in question are probably Regnault, H. V. Recherches sur la dilatation des gaz. *Ann. chem. phys.* 1842, 4, 4–67; *ibid.* 1842, 5, 52–83; and Sur la loi de compressibilité des fluides élastiques. *Compt. rend.* 1846, 23, 787–798.
7. Reference 2b, footnote, p 22.

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Questions should be addressed to:

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 Department of Chemistry
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 jensenwb@email.uc.edu