С. Торайғыров атындағы Павлодар мемлекеттік университетінің
ҒЫЛЫМИ ЖУРНАЛЫ

НАУЧНЫЙ ЖУРНАЛ
Павлодарского государственного университета имени С. Торайгырова

ПМУ ХАБАРШЫСЫ

Энергетикалық сериясы
1997 жылдан бастап шығады

ВЕСТНИК ПГУ

Энергетическая серия
Издается с 1997 года

№ 2 (2017)

Павлодар

UDC 621.1:621.43

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GAS CONSTANTS: SPECIFIC, MOLAR, VOLUMETRIC AND MOLECULAR

The systematization of gas constants is given. The volumetric gas constant and the corresponding equation of state allowing to determine unambiguously the volume and density of an ideal gas at normal physical conditions are entered.

Keywords: gas constants, Boltzmann constant, volumetric gas constant, the equation of state of an ideal gas.

INTRODUCTION

The equation which connects the pressure p, the volume V and the temperature T of a thermodynamic system is called as an equation of state of a thermodynamic system: $f(p, V, T) = 0$. Historically the equation of state was received, proceeding from laws of Boyle and Gay-Lussac. Let's consider some methods of receiving an equation of state. It is noted in work [1, p. 3]:

The three empirical laws were as follows:

1 Marriott's law, which was anglo-saxonized into Boyle's law by Tait, asserts that at constant temperature the product of the pressure and volume remains constant

$$pV = \text{const}. \tag{1}$$

2 Gay-Lussac's law, which again was anglo-saxonized into Charles's law by the same Tait, states that for all permanent gases, the empirical temperature t is proportional to the fractional increase in volume at constant pressure,

$$t = \frac{1}{\alpha}\frac{V - V_0}{V_0}, \tag{2}$$

Where α is a constant, known as the coefficient of thermal expansion, which was same constant for all permanent gases.

Combining (1) and (2) gives

$$pV = p_0 V_0 \alpha (1/\alpha + t). \tag{3}$$

The unit of mass is known as the gram-molecule, or simply «mol». A mole is just molecular weight in grams. If there are n moles of substance, the specific molal volume is $v = V/n$. If we call

$$R = p_0 V_0 \alpha, \tag{4}$$

then (3) can be written as

$$pV = nR(1/\alpha + t), \tag{5}$$

and R is referred to as the gas constant. We will normally refer to one mole of substance.

3. Avogadro's number, which is the third of the three empirical laws, says that the molal volume, v, is nearly the same for all permanent gases under «normal» conditions of $p = 1$ atm, $t = 0$ °C, and $v_0 = 22{,}41$ см³. Therefore, the gas constant is also universal. One mole of any substance contains the same number of molecules N_A, known as Avogadro's number. It is roughly 6×10^{23}, and Boltzmann's constant, which was actually discovered by Plank, is the gas constant per molecule, $\kappa = R/N_A$».

In [2, p. 26] is noted:

«It was found that three parameters (pressure, volume and temperature) satisfy, to a good approximation, the following equation:

$$pV = B(t_C + 273.15\,^{\circ}\mathrm{C}), \tag{6}$$

where B is constant for a given amount of gas. Moreover, it was shown that

$$B = nR,$$

where n is the number of moles of the gas, and $R = 8.31472\ \mathrm{JK^{-1}mol^{-1}}$ is called the *gas constant*. It is easy to recognize that the temperature in Eq. (6) is actually expressed in the Kelvin scale, hence, (6) can be rewritten as follows:

$$pV = nRT».$$

In [3, p. 75] is noted:

«It has been observed experimentally that, to a close approximation, a very-low-density gas behaves according to the ideal-gas equation of state

$$pV = n\overline{R}T, \quad p\overline{v} = \overline{R}T, \tag{7}$$

in which n is the number of kmol of gas, or

$$n = \frac{m}{M} \quad \frac{\mathrm{kg}}{\mathrm{kg/kmol}}. \tag{8}$$

In Eq. (7) $\overline{R}$ is the universal gas constant, the value of which is, for any gas, $\overline{R} = 8.3145 \frac{\mathrm{kJ}}{\mathrm{kmol\,K}}$ and T is the absolute (ideal-gas scale) temperature in kelvins (i.e., T(K) = T(°C) + 273.15). It is important to note that T must always be the absolute temperature whenever it is being used to multiply or divide in an equation.

Substituting Eq. (8) into Eq. (7) and rearranging, we find that the ideal-gas equation of state can be written conveniently in the form

$$pV = mRT, \quad pv = RT,$$

where

$$R = \frac{\overline{R}}{M}$$

in which R is a different constant for each particular gas».

The equation of state is written in textbook [4, p. 10] in the form

$$pv = RT.$$

The specific gas constant R, J/(kg.K), is described by equation $R = \frac{R_M}{M}$, in which $R_M = 8314$ J/(kmol.K), is the universal (molar) gas constant; M is the molar mass of gas, kg/kmol.

As it follows from the contexts, when writing the equation of state ideal gas, the gas constants are used for the whole body, for one mole, and for one kilogram of substance. At the same time various gas constant are often denoted by the same symbol R, and the technical terms of these magnitudes are not systematized. The systematization of the gas constants is included below.

MAIN PART

The following systematization of physical quantities is accepted depending on the selected portion of substance in science (designations of quantities are accepted according to recommendations about development of uniform system of alphabetic designations of quantities [5]).

It is accepted to call the ratio of any quantity B to the body mass of m a specific quantity and to use for her designation a lower case letter of the main symbol

$$b = \frac{B}{m}. \tag{9}$$

It is accepted to call the ratio of any quantity B to the amount of substance μ a molar quantity and to designate a symbol

$$B_\mu = \frac{B}{\mu}. \tag{10}$$

It is accepted to call the ratio of any quantity B to the volume of substance V a volume quantity and to designate a lower case letter of the main symbol with a prime.

$$b' = \frac{B}{V}. \quad (11)$$

It is accepted to call the ratio of any quantity B to the particle number N (molecules) a molecular quantity and to designate a symbol

$$B_N = \frac{B}{N}. \quad (12)$$

Such systematization (9)–(12) is conducted for heat capacities, at that the following types of heat capacity are introduced:

$C_{body} = \frac{Q}{\Delta T}$, – heat capacity of body, J/K;

$c = \frac{C_{body}}{m} = \frac{Q}{m\Delta T}$ – specific heat capacity, J/(kg.K);

$C_\mu = \frac{C_{body}}{\mu} = \frac{Q}{\mu\Delta T}$ – molar heat capacity, J/(mol.K);

$c' = \frac{C_{body}}{V_0} = \frac{Q}{V_0\Delta T}$ – volumetric heat capacity, $J/(m^3 \cdot K)$;

$C_N \equiv c_1 = \frac{C_{body}}{N} = \frac{Q}{N\Delta T}$ – molecular heat capacity, J/K.

It has been established by combining the gas laws ideal gas Gay-Lussac and Boyle-Marriott that the ratio of product of the pressure on the volume to the thermodynamic temperature is a constant magnitude. We will call this constant, since it refers to the entire body (system), the gas constant of body (gaseous body) and will denote R_{body} (J/K)

$$\frac{pV}{T} = \text{const} = R_{body}.$$

The general equation of the ideal gas follows from here

$$pV = R_{body}T. \quad (13)$$

We, by comparing (3) and (13), conclude that under R in (4) it is necessary to understand the gas constant of a body R_{body}, and in the expression (5) there is already other gas constant – molar and therefore they cannot be designated by one symbol R.

The origin of thermodynamics associated with the name of Carnot, who published in 1824 his work «Memoir about a driving force of fire and about machines capable to develop this force». In his memoir Carnot for the first time brings together into a single equation the laws of Boyle and Gay-Lussac, which he recorded in the form of [6, p. 138].

$$p = N(t + 267)/V, \quad (14)$$

or in modern writing $pV = R_{body}(t + 273{,}15) = R_{body}T$, where N is «the constant quantity depending on the weight of steam and the chosen units»; t is Celsius temperature; 267 is the reciprocal number to coefficient of the volumetric expansion of gases 1/267 (by data for that time).

Carnot died, and did not hear any response to his work. Fact sad but not single in the history of science. In 1834 Klapeyron processed Carnot's work and almost under the same name ("Memoir about a driving force of fire") published in works of Polytechnical school in Paris.

Clapeyron writes in his memoir united equation in the form

$$pV = A(t^o + 267), \quad (15)$$

where A is a constant for a given mass of gas. He calls this equation the «equation of state of the Gay-Lussac-Marriott», and it is widely used in this study.

It is obvious that Klapeyron's equation (15) is identical to Carnot's equation (14). Klapeyron, being engaged the theory of Carnot in his work , does not say anywhere that the author of the first integrated equation is Carnot, however, and to himself he does not attribute it. Carnot's book quickly became a rare book and very few people were familiar with her. Therefore no wonder that the equation of the integrated law of Boyle-Mariott-Gay-Lussac began to attribute Klapeyron. It would be more correct to call the ideal gas equation, which is written down through gas constant of body, Carnot-Clapeyron's equation.

According to the general expressions (9)–(12) the following gas constants are entered into thermodynamics:

– specific gas constant, J/(kg.K)

$$R = \frac{R_{body}}{m} = \frac{pV}{mT}; \quad (16)$$

– molar (universal) gas constant, J/(mol.K),

$$R_\mu = \frac{R_{body}}{\mu} = \frac{pV}{\mu T} = \frac{pV_\mu}{T}; \quad (17)$$

– «volumetric gas constant»[1], $J/(m^3 \cdot K)$,

$$R' = \frac{R_{body}}{V_o} = \frac{pV}{V_o T}; \qquad (18)$$

– molecular gas constant, J/K.

$$R_N = \frac{R_{body}}{N} = \frac{pV}{NT}. \qquad (19)$$

Connection between gas constants can be established if in relations (16)–(19) R_{body} to replace on $Rm = R_\mu \mu = R'V_o = R_N N$:

$$R = R_\mu \mu / m = R_\mu / M; \qquad (20)$$

$$R' = R_\mu \mu / V_o = R_\mu / V_{\mu o}, \; R' = Rm/V_o = \rho_o R \qquad (21)$$

$$R_N = R_\mu \mu / N = R_\mu / k_A = k_B; \qquad (22)$$

where $V_{\mu o} = V_o / \mu$ is molar volume of ideal gas given to a normal physical conditions (p_o = 101325 Pa, T_o = 273,15 K);

$k_A = N / \mu = N_\mu$ is Avogadro constant (molar number of particles), which value depends on the value of the unit amount of substance (1 mol or 1 kmol = 1000 mol);

$N_A = 6{,}022140857 \times 10^{23}$ is Avogadro number[2], numerically equaling to constant Avogadro for 1 mol [7].

According to the Avogadro's law, with the same pressure and temperatures, molar volumes of different gases are also identical. At normal physical conditions molar volume is equal $V_{\mu o} = 22{,}413962 \times 10^{-3}$ m^3/mol [7]. The value of molar gas constant is determined by known molar volume from the expression (17)

$$R_\mu = \frac{p_o V_{\mu o}}{T_o} = \frac{101325 \cdot 22{,}413962 \cdot 10^{-3}}{273{,}15} = 8{,}3144598 \text{ J/(mol·K) [7]}.$$

Since the molar volume $V_{\mu o}$ is identical for all gases, then and the molar gas constant R_μ is constant for all gases, from here and it is original name – the universal gas constant.

The specific gas constant is given by (20), for example, for air M = 28,966 kg/kmol [8],

$$R = R_\mu / M = 8314{,}4598 / 28{,}966 = 287{,}04 \text{ J/(kg·K)}.$$

1 The term "volumetric gas constant" and quantity itself R' are introduced for the first time.

2 Avogadro number NA, whose value consistently, often identified with the Avogadro constant k_A, the value of which depends on the adopted unit, and represent the same symbol N_A. This introduces uncertainty when considering the formulas with these quantities.

The value of the volumetric gas constant is determined from the expression (21)

$$R' = R_\mu / V_{\mu o} = 8{,}3144598 / 22{,}413962 \cdot 10^{-3} = 370{,}950027 \text{ J/(m}^3 \cdot \text{K)}.$$

Because here it is taken the ratio of the two magnitudes identical for all gases, the volumetric gas constant could be called the «second universal gas constant», that makes the term «universal gas constant» ambiguous and it is not recommended to be applied.

From (22) it follows that the molecular gas constant is defined as the ratio of two constants and, therefore, is itself a "universal" constant, which is called Boltzmann's constant $R_N = k_B = R_\mu / k_A = 8{,}3144598 / 6{,}022140857 \cdot 10^{23} = 1{,}38064852 \cdot 10^{-23}$, J/K [7]. Consequently, the Boltzmann constant kB, in accordance with the expressions (19) and (22), is none other than the molecular gas constant, determined by the ratio of gas constant of the body to the number of gas molecules (19).

Volumetric quantities (for example, c'_p, h'), along with the volume V_o, is used in the theory of combustion, as well as densities component products of combustion under normal physical conditions, which can be determined from the relation (21) $\rho_{oi} = R' / R_i$.

For example, the air density under the normal physical conditions

$$\rho_{ов} = R' / R_в = 370{,}95 / 287 = 1{,}2925 \text{ kg/m}^3.$$

The traditional calculation gives

$$\rho_{ов} = \frac{p_o}{R_в T_o} = \frac{101325}{287 \cdot 273{,}15} = 1{,}2925 \text{ kg/m}^3.$$

CONCLUSION

1 The classification of gas constants (body, specific, volumetric, molar, molecular) depending on the accepted portion of substance is given.

2 The new «volumetric gas constant», identical to all gases, – «the second universal gas constant» – is entered.

3 The new equation of state for perfect gas $pV = V_o R' T$ allowing to determine directly the volume of gas V_o and its density $\rho_o = R' / R$ at standard physical conditions is received.

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Material received on 05.06.17.

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Газ тұрақтылары: меншікті, көлемдік, молярлық және молекулярлық

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Материал 05.06.17 баспаға түсті.

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Газовые постоянные: удельная, объёмная, молярная и молекулярная

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имени С. Торайгырова, г. Павлодар.
Материал поступил в редакцию 05.06.17.

Газ тұрақтыларын жүйелеу келтірілген. Көлемдік газ тұрақтысы енгізілуде және теңдеуің жағдайына сәйкес келетін, көлемді анықтауға мүмкіндік беретін және қалыпты физикалық жағдайларға газ тығыздық анықтау.

Приводится систематизация газовых постоянных. Вводится объёмная газовая постоянная и соответствующее уравнение состояния, позволяющее однозначно определять объём и плотность идеального газа при нормальных физических условиях.