ISSN : 0974 - 7524

Volume 9 Issue 4



Short Communication

IEMISTRY

An Indian Journal

PCAIJ, 9(4), 2014 [151-152]

Explanation of an ideal gas paradox

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ABSTRACT

In some papers, the following paradox was proposed. The description of the internal energy of a simple gas is based historically on free expansion experiments and univariable equations of state. According to these equations, the internal energy of simple monatomic, diatomic, and polyatomic gases can be expressed only as a function of temperature. The authors declared that it was a wrong approach because a thermodynamic state cannot depend on one variable but must depend on two. They claim that multivariable equations of state derived from composite functions must be used instead which say that the internal energy of these gases can in each situation also be expressed only as a function of volume and pressure. In the present paper, an attempt to resolve this paradox is made. This paper could be of interest to a broad range of chemists and chemical engineers who use thermodynamics of gases in their work. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Ideal gas; Real gas; Equation of state; Internal energy; Mathematical definition of function.

INTRODUCTION

In^[1-4] a paradox in the ideal gas was declared. The gas law is

$$\mathbf{PV} = \mathbf{RT} \tag{1}$$

where P is pressure, V is volume, R is the universal gas constant, and T is temperature. Two variables are necessary to determine a property of a gas, such as its internal energy. From the kinetic theory, the internal energy of the ideal gas is

$$U(T) = \frac{3}{2}RT$$
 (2)

The paradox is that the energy depends only on one variable, T, but must depend on two. From Eqs. (1) and (2) it follows that

$$U(P, V) = \frac{3}{2}PV$$
(3)

Here the energy depends on two variables and the authors^[1-4] concluded that Eq. (2) is wrong. In^[4] it was mathematically proven that the internal energy U can be represented as two different functions, $U_1(T)$ and $U_2(P,V)$; the first one depending on temperature only and the second one depending on pressure and volume only.

This paradox is valid also for real gases because in a wide range of temperatures and pressures, they only minimally deflect from the ideal gas. For example, the molar volumes of argon, helium, hydrogen, nitrogen, oxygen, and methane deviate at about 0.1 percent of 22.414 liters at standard temperature and pressure and

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even less for higher temperatures and lower pressures. For argon, the difference between the theoretical and experimental heat capacity is less than 0.1 percent^{[1–} ^{3,5]}. For real gases, there will be a weak dependence of thermodynamic properties on volume in Eq. (2) and strong dependence on volume in Eq. (3).

RESULTS AND DISCUSSIONS

The explanation of the paradox begins by acknowledging that the internal energy function depends on the process. For some processes, the internal energy depends on the volume and for some it does not. Consider two volumes, V_1 and V_2 , $V_2 > V_1$, each containing a mole of the ideal gas. The energies of the gas in both volumes are equal and given by Eq. (2). If one introduces a quantity of heat δQ into each of the volumes, the energies of gas again become equal and described by Eq. (2) but with a higher temperature. These are correct results and there is no mistake in Eq. (2). If, however, one compresses the volumes, then the process must be described by Eq. (3). Equation (2) generally is not valid. There are thus two types of processes. In the first one, the volume of the system is not changed by compression or mechanical expansion and, in the second one, the system is compressed or expanded mechanically. Both types are described by different internal energy functions. There is not a universal internal energy function. According to the rigorous mathematical definition of function, the internal energy must constitute two different functions which depend on different variables^[4].

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