

Study of thermodynamic parameters of hydrogen gas by grapho-analytic method

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Abstract

The grapho-analytical method is expected to guarantee more precise outcomes when applied to the analysis of (T, V) , $P = \text{const}$, $(P, 1/V)$, $T = \text{const}$ diagrams for gases. Results for hydrogen gas (H_2) give outcomes principally distinguished from similar researches for carbon dioxide (CO_2), oxygen (O_2), argon (Ar), helium (He), neon (Ne) and other gases.

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1. Introduction

Thermodynamic parameters are determined theoretically or empirically. When determined by theoretical methods, the values of the parameters differ appreciably from the actual values, therefore the empirical methods are chosen in preference to the theoretical ones in many industrial applications. However, the high cost of the experiments and other related technical difficulties remain the major obstacles as to their performance.

Recently, more effective and faster alternative methods have been developed. The grapho-analytical method remains one of the most widely used method [1–3,14].

In this article, we apply the grapho-analytical method to investigate the (T, V) , $P = \text{const}$ and $(P, 1/V)$, $T = \text{const}$ diagrams for different gases.

The grapho-analytical method applies to the solid, liquid and gaseous phases and provides accurate results concerning the system's equilibrium state, phase transitions, critical

parameters (T_{cr} , P_{cr} , V_{cr}), temperatures of melting, boiling and freezing (T_{th} , T_{b} , T_{f}), to name but a few.

Temperature plays an important role in everyday use, in industrial and scientific researches. Because temperature is the most accessible thermal concept, its measurement have required the development of diverse thermometers (mercury, alcohol and others operating on the basis of water and gas) used in different fields of application.

A gas-pressure thermometer, based on the perfect gas law, is widely used for measurements and calibrations. Its scale is identical to the thermodynamic scale of temperature, which is independent of the thermometric substance. Standard gas-pressure thermometers use hydrogen (H_2) as a thermometric substance [1]. If we assume that hydrogen follows the perfect gas law, then, at constant volume and density, the pressure of H_2 is proportional to its temperature, which is also the temperature of the body in contact with the thermometer. The melting (0°C) and boiling (100°C) temperatures of water are taken as reference points. These points are indicated on the diagram (Fig. 1), where P_0 and P_{100} are the thermometer gas pressures at the temperatures of melting ice (0°C) and boiling water (100°C),

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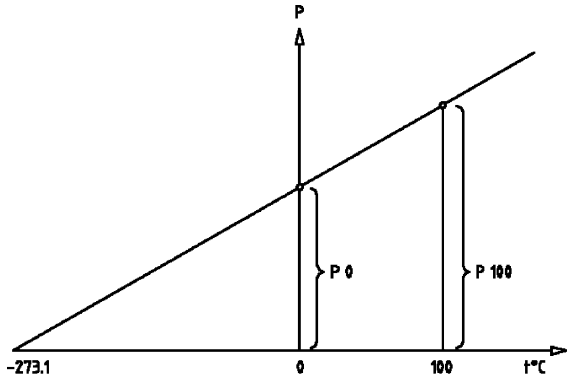


Fig. 1. Determination of the absolute zero of temperature by a graphical method.

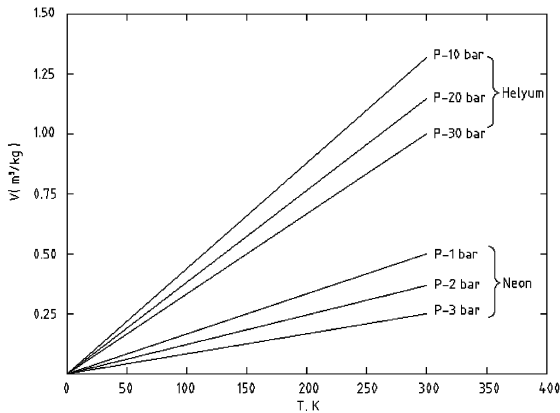


Fig. 2. (T, V) , $P = \text{const}$ diagrams for He and Ne.

respectively. These melting and boiling temperatures of water are measured when the pressure on water is kept at 760 mm of a column of mercury.

The line through the points P_0 and P_{100} is extended until it meets the t -axis.

The line is described by the equation

$$t = \frac{P - P_0}{P - P_{100}} * 100. \tag{1}$$

It intersects the t -axis at -273.1°C , which corresponds to absolute zero on the absolute thermodynamic scale of temperature [1].

The grapho-analytical method has been applied to determine properties of gaseous matter [2–5,13].

Fig. 2 shows the plots of the specific volume versus the absolute temperature for helium (He) and neon (Ne) at different pressures. As a result of our studies, all isobars ($P = \text{const}$) intersect at the origin $(0,0)$ on a (T, V) diagram. Similar studies applied to the case of gaseous hydrogen show different outcomes.

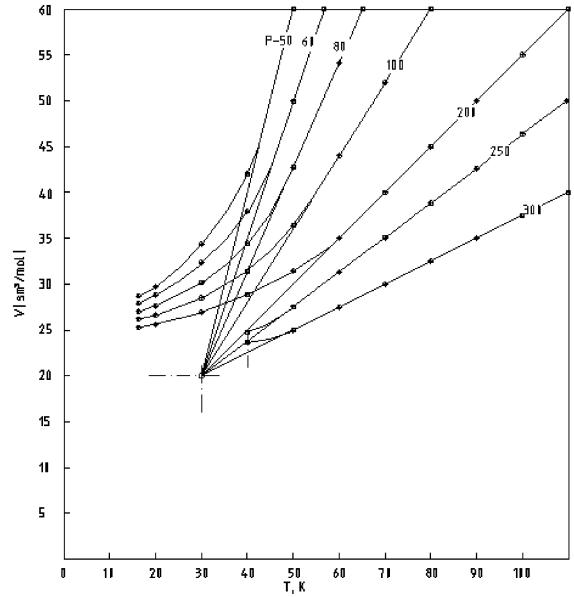


Fig. 3. (T, V) , $P = \text{const}$ diagram for hydrogen.

2. Analysis of hydrogen properties by the grapho-analytical method

Hydrogen is considered as the energy of the 21st century [6], besides being a standard gas. From this point of view, a detailed examination of its properties is provided in [7].

Based on empirical data extracted from [8], a plot of the specific volume versus the absolute temperature for H_2 is sketched in Fig. 3 for different values of the pressure. As the temperature drops, the volume of H_2 departs from the linear dependance law, observed in the cases of He and Ne, to a parabolic dependance.

In this case, the linear extrapolation of hydrogen curve, as well as the curve of other gases, can be applied only for definite ranges of the temperature.

For example, linear extrapolation of the isobar $P = 50$ is possible only for temperatures higher than 44 K, and on the isobar curve $P = 60$ —for temperatures higher than 48 K. The line becomes a parabola for $16 \text{ K} < T < 44 \text{ K}$ whose shape depends on the value of the pressure.

Furthermore, the extrapolated lines meet in the range $(T = 33.0 \pm 0.5 \text{ K}, V = 21.0 \pm 1.0 \text{ cm}^3/\text{mol})$ which does not include the origin of the (T, V) -plane.

Taking into account this peculiarity of hydrogen gas, the isotherms on a $(P, 1/V)$ diagram are sketched in Fig. 4. At $T < 20 \text{ K}$ the hydrogen consists only of one modification “para-hydrogen” [8,9]. Isotherms in $(P, 1/V)$ coordinates demonstrate the linear character for this temperature’s range under the considered pressure interval. As $T \rightarrow 0$, the isotherms approach the (small) finite values of density $(1/V)$ that are different from each other (Fig. 5).

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