

GAS ANALYSIS OF TERNARY MIXTURES FOR PROCESS-INSTRUMENTATION USING NON-SELECTIVE SENSORS

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Abstract

A concept for a multicomponent gas analyzer is shown, working without selective sensors. Each of the used sensors detects one physical quantity. With the physical rules for the quantities of a mixture we get a third order set of equations, describing the relation between the quantitative combination and the data. This set of equations will be solved with a microcomputer.

Introduction

A typical method making use of a nonselective sensor is the measurement of the thermal conductivity [1]. It is used for analysing binary gas-mixtures in process instrumentation.

Instead of the thermal conductivity you can also measure the density, the viscosity, the adiabatic exponent or the molar heat. All these quantities are describing the gaskinetic characteristics of a molecule. Our idea was to analyse a multicomponent gas mixture by measuring some of these quantities. However, it can be shown, that there is an upper limit for the maximum number of different gases that can be analysed. Another problem is the selection of well suited quantities, as mentioned above, to guarantee an efficient measurement system. Therefore it is necessary to investigate the gaskinetic relationships between the macro- and microscopic entities.

Gaskinetics of pure gases

The density ρ of a gas is given by the mass m of a molecule multiplied by the number of molecules per volume N [2]:

$$\rho = m \cdot N.$$

The adiabatic exponent κ is the molar heat at constant pressure c_p divided by the molar heat at constant volume c_v . The molar heats are functions of the

number of degrees of freedom f of a molecule and the gas constant R . So the adiabatic exponent is a function only of the number of degrees of freedom.

$$\kappa = \frac{c_p}{c_v} = \frac{(1+f/2)R}{f/2 R} = 1 + 2/f.$$

The thermal conductivity as well as the viscosity are transport phenomena. The viscosity is given as:

$$\eta = 1/3 N m v l$$

with the mean thermal velocity:

$$v = (3 k T/m)^{1/2}, \quad \begin{array}{l} k: \text{ Boltzmann constant} \\ T: \text{ Temperature} \end{array}$$

and the mean free path:

$$l = 1/(\sqrt{2} \pi N 4 r^2). \quad r: \text{ gaskinetic radius}$$

The formula for the thermal conductivity λ is similar to the one for the viscosity. It contains the molar heat c_v instead of the mass. It can also be expressed as one half of the number of degree of freedom times the gas constant:

$$\lambda = 1/3 N c_v v l \quad \text{or} \quad \lambda = 1/3 N f/2 R v l.$$

Obviously, the macroscopic quantities of a gas: the density, the viscosity, the thermal conductivity, the adiabatic exponent and the molar heat, are completely determined by the 3 microscopic entities: mass, gaskinetic radius and number of degrees of freedom.

Considering the continuity equation, sum of x_i equals 1, with x_i being the fraction of each gas from the whole mixture, the maximum number of components that can be analysed is 4.

Gaskinetics of mixtures

As shown above, the microscopic quantities m , r , f , completely characterize a molecule. To accomplish the multicomponent gas analyzer, it is essential to know how the measured macroscopic quantities of a gas mixture are related to the microscopic quantities of the pure gases.

From gaskinetic theory [2] we get:

$$\lambda = 1/6 R \sum_i N_i f_i v_i l_i,$$

$$\eta = 1/6 R \sum_i N_i f_i v_i l_i.$$

Where v_i is the same as the one for pure gases. But the l_i are nonlinear functions of the N_i , R_i , m_i , of all components:

$$l_i = 1 / \sum_j (R_i + R_j)^2 (1 + m_i/m_j)^{1/2} N_j.$$

For the adiabatic exponent, we get a further nonlinear function:

$$\kappa = \frac{\sum x_i c_{pi}}{\sum x_i c_{vi}} = \frac{\sum (1 + f_i/2) x_i}{\sum f_i/2 x_i}.$$

The density of a mixture is a linear function of the fractions:

$$\rho = \sum m_i N_i \quad \text{or} \quad \rho = \sum \rho_i x_i.$$

The implemented method for ternary gas analysis

We can see from the above considerations that 2 quantities have to be measured for the analysis of a ternary mixture. The first one is the density, which has a linear relation to the densities of the pure gases and the fractions. The other quantities obey nonlinear equations, whose solution with a microcomputer needs a very long time.

However, defining a mean number of degrees of freedom f_m , for a mixture, we get a further linear equation:

$$f_m = \sum x_i f_i$$

yields:

$$\kappa = 1 + 2/f_m.$$

So the needed f_m can be calculated from the measured adiabatic exponent as:

$$f_m = 2 / (\kappa - 1).$$

Eventually we get a system of 3 linear equations:

$$x_1 + x_2 + x_3 = 1,$$

$$\rho_1 x_1 + \rho_2 x_2 + \rho_3 x_3 = \rho,$$

$$f_1 x_1 + f_2 x_2 + f_3 x_3 = f_m,$$

with the solution:

$$x_3 = \frac{(f_m - f_1)(\rho_2 - \rho_1) - (\rho - \rho_1)(f_2 - f_1)}{(f_3 - f_1)(\rho_2 - \rho_1) - (\rho_3 - \rho_1)(f_2 - f_1)},$$

$$x_2 = \frac{\rho - \rho_1}{\rho_2 - \rho_1} - \frac{\rho_3 - \rho_1}{\rho_2 - \rho_1} x_3$$

$$x_1 = 1 - x_3 - x_2.$$

The results contain many constant factors, which depend only on the parameters of the pure gases. Therefore all necessary calculations can be easily done, using a microcomputer.

The κ -meter

The adiabatic equation $PV^\kappa = \text{const.}$ describes the relation between the pressure P and the volume V of a gas for adiabatic changes of state. For small changes of pressure ΔP and volume ΔV we get a linearized equation:

$$\frac{\Delta P}{P_0} = -\kappa \frac{\Delta V}{V_0} \quad \text{or} \quad \kappa = -\frac{\Delta P}{\Delta V} \frac{V_0}{P_0}.$$

In the measurement chamber (Fig. 1) an oscillating membrane is generating fast periodic changes in volume and the changes of pressure are measured. The frequency is chosen high enough, to avoid heat transfer between the gas and the chamber.

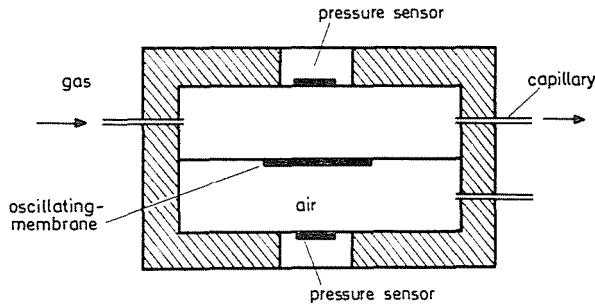


Fig. 1. Measurement chamber of the κ -meter

The absolute pressure P_0 and the amplitude of the changes of the volume can be eliminated by means of a reference chamber, containing air as reference gas. The oscillating membrane is between the measurement and the reference chamber. So the magnitude of the changes of volume is the same in both chambers. With the known adiabatic exponent for air and the measured pressures the adiabatic exponent can be calculated:

$$\frac{\kappa}{\kappa_{\text{air}}} = \frac{\Delta P}{\Delta P_{\text{air}}} \quad \text{or} \quad \kappa = \kappa_{\text{air}} \frac{\Delta P}{\Delta P_{\text{air}}}.$$

To achieve a continuous measurement system, the chamber is supplied with a constant flow of the gas mixture to be analysed. However, the inlet and outlet of the chamber is made through capillaries, to obtain a virtually closed system. Their resistance to flow, together with the chamber volume are forming a pneumatic low-pass. The geometric dimensions are chosen so, that the cutoff frequency of this low-pass is far below the operating frequency.

Measurement of gas density in a pulsating flow field

In the detector (Fig. 2) the gas is accelerated by an oscillating membrane and a microphone is measuring the pressure gradient. Then the imaginary part of the signal is proportional to the density of the gas and the known frequency of oscillation [3].

Modulation with a square wave of the same frequency and 90 degrees phase shift gives an analog output signal which is proportional to the density of the gas.

To be independent of the atmospheric pressure, the system also makes use of a reference chamber.

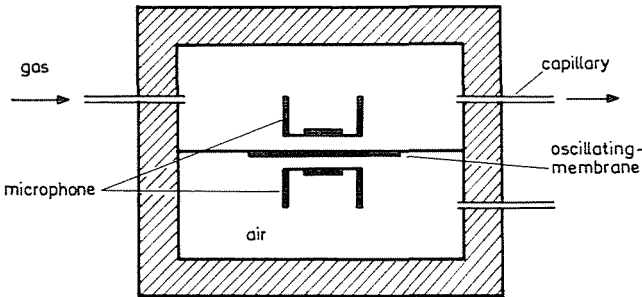


Fig. 2. Measurement chamber of the density-meter

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