FTD-MT-24-1860-71

FOREIGN TECHNOLOGY DIVISION

AIR FORCE SYSTEMS COMMAND

ANALYSIS OF THE COMPOSITION OF GAS BY THE THERMAL CONDUCTIVITY METHOD. PHYSICAL PRINCIPLES

by

L. Ye. Kocherov and M. D. Shutov

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11

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Foreign Technology Division Air Force Systems Command U. S. Air Force	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3. REPORT TITLE

ANALYSIS OF THE COMPOSITION OF GAS BY THE THERMAL CONDUCTIVITY METHOD. PHYSICAL PRINCIPLES

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Translation

5. AUTHOR(S) (First name, middle initial, last name)

Kocherov, L. Ye. and Shutov, M. D.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
1968	6	6

8a. CONTRACT OR GRANT NO. F33615-71-C-1182 b. PROJECT NO. c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) FTD-MT-24-1860-71 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Foreign Technology Division Wright-Patterson AFB, Ohio

13. ABSTRACT

The theory of anal. of gas mixts. based on the measurement of their thermal cond. is discussed. The dependence of thermal cond. coeff. of gas mixts. on their compn. and temp. is described. Structural design of sensing elements of thermal cond. gas analyzers are also described.

DD FORM 1 NOV 65 1473

UNCLASSIFIED

Security Classification

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Thermal Conductivity Hydrogen Helium						

UNCLASSIFIED

Security Classification

FTD-MT-24-1860-71

EDITED MACHINE TRANSLATION

ANALYSIS OF THE COMPOSITION OF GAS BY THE THERMAL CONDUCTIVITY METHOD. PHYSICAL PRINCIPLES

By: L. Ye. Kocherov and M. D. Shutov

English pages: 6

Source: Entsiklopediya Izmereniy, Kontrolya i Avtomatiki (Encyclopedia of Measurements, Monitoring, and Automatic Equipment), No. 11, 1968, pp. 5-6.

Translated by: J. Miller

UR/0000-68-000-011

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ANALYSIS OF THE COMPOSITION OF GAS BY THE THERMAL CONDUCTIVITY METHOD. PHYSICAL PRINCIPLES

L. Ye. Kocherov and M. D. Shutov

Special Design Bureau for Analytical Instrument Construction of the Academy of Sciences of the USSR, Leningrad

One of the most widespread and universal methods of gas analysis is the method of thermal conductivity, based on a comparison of the thermal conductivities of gases [1-3]. The limits of applicability of the method of thermal conductivity are determined by the various values of the coefficients of thermal conductivity of the different gases (see the table).

The coefficients of thermal conductivity of gases depend essentially on the temperature. In simplified form, this dependence is expressed by the binomial

$$\lambda_t = \lambda_0(1 + \beta t), \qquad (1)$$

where λ_0 and λ_t are the coefficients of thermal conductivity of gas at temperatures 0 and t °C; β is the temperature coefficient of thermal conductivity.

The temperature coefficients of thermal conductivity differ for different gases and depend on the temperature. This dependence is treated as a piecewise-linear dependence, and we use the average values of the temperature coefficients of thermal conductivity for a certain

Coefficients of thermal conductivity of gases at 0°C, temperature coefficients of thermal conductivity*.

Gas	$\lambda \cdot 10^4$, W/m·deg	$\beta \cdot 10^4$, 1/deg (in the interval 0-100°C)
nitrogen	243	28
ammonia	218	48
argon	167	30
acetylene	190	48
butane	135	72
hydrogen	1740	27
air	244	28
helium	1457	18
sulfur dioxide	85.4	—
carbon dioxide	146	48
methyl iodide	47.3	—
oxygen	246	28
xenon	51.9	—
methane	302	48
carbon monoxide	236	28
pentane	130	—
propane	150	73
hydrogen sulfide	131	—
chlorine	78.7	—
chloroform	66	—
ethane	182	65
ethylene	175	74

*Detailed and currently more reliable values for the coefficients of thermal conductivity of many gases and the constants entering the equations for their temperature dependences are given in the "Handbook of Chemistry," second edition, vol. 4 (Izdatel'stvo "Khimiya," 1967), section "Gas analysis" (compiled by D. L. Orshanskiy, M. L. Rabinovich, and N. F. Yablonskaya), pp. 576-579 (Editor's note).

temperature range, for example, 0-100°C, as is done in the table. Differences in the values of the temperature coefficients of thermal conductivity have the result that at certain specified temperatures (different for different gases) the values of the coefficients of thermal conductivity of gases become equal. For example, the coefficient of thermal conductivity of air is equal to that for carbon dioxide at 325°C, for acetylene at 100°C, and for ammonia at 65°C.

For a gaseous mixture of nonpolar or polar gases, distinguished by their molecular weights, the coefficient of thermal conductivity is defined as follows [4]:

$$\lambda_{cm} = \frac{c_1\lambda_1\sqrt[3]{M_1} + c_2\lambda_2\sqrt[3]{M_2} + \ldots}{c_1\sqrt[3]{M_1} + c_2\sqrt[3]{M_2} + \ldots}, \qquad (2)$$

where λ_1, λ_2, ... are the coefficients of thermal conductivity of the first, second, etc., components of the gas mixture; c_1, c_2, ... are the concentrations of the first, second, etc., components, in volume percents; M_1, M_2, ... are the molecular weights of the first, second, etc., components.

Mixtures of hydrogen or helium with other gases are typical mixtures (Fig. 1, curve 1).

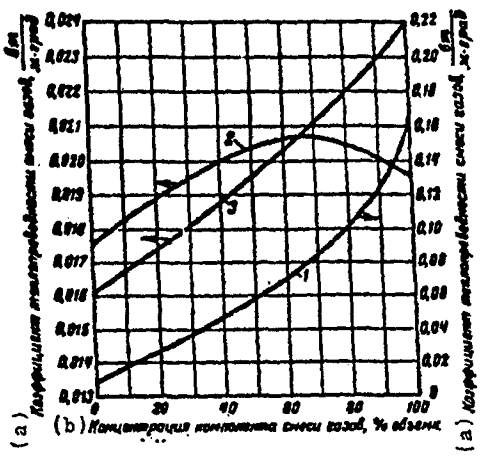

Fig. 1. Dependence of the coefficients of thermal conductivity of gas mixtures on the concentration of the second component. 1 — $CO_2 + H_2$; 2 — $C_6H_6 + CH_3OH$ (vapors); 3 — $Ar + N_2$

KEY: (a) coefficient of thermal conductivity of gas mixture, W/m·deg; (b) concentration of component of gas mixture, vol. %

If in a gas mixture consisting of nonpolar gases there is a polar component, its coefficient of thermal conductivity changes greatly as a function of the concentration of the polar component (Fig. 1, curve 2). In this case, the coefficient of thermal conductivity of the gas mixture is described by the formula

$$\lambda_{cm} = (c_1\lambda_1 + c_2\lambda_2 + \ldots)\left(1 + \frac{c_n - c_n^2}{3.5}\right). \qquad (3)$$

where c_n is the concentration, in vol. %, of either all polar or all nonpolar components.

A mixture of water vapors or ammonia with air is a typical mixture for this case.

Finally, in the case of a gas mixture consisting of polar or nonpolar components whose molecular weights are close, the coefficient of thermal conductivity is approximately subject to the additive law (Fig. 1, curve 3):

$$\lambda_{см} = c_1\lambda_1 + c_2\lambda_2 + \dots \qquad (4)$$

All of the above formulas (2)-(4) are empirical formulas.

Thus, the dependence of thermal conductivity of a gas mixture on the concentration of the components in the mixture is of an unambiguous nature only for binary and pseudobinary mixtures,[1] which significantly reduces the sphere of applicability of gas analyzers with respect to thermal conductivity. To expand the region of applicability of the method of thermal conductivity to multicomponent gas mixtures, special measures are taken [5] which make it possible to a considerable extent to increase the selectivity of the gas analyzers operating according to this method.

In thermal-conductivity gas analyzers we compare the coefficients of thermal conductivity of the analyzed gas mixture and a certain comparative gas mixture. The method for determining the absolute value of the coefficient of thermal conductivity is not used, due to its experimental complexity and low accuracy. The coefficients of thermal conductivity of gases are determined with an error of several percent, while modern recording gas analyzers have a change in the coefficient of thermal conductivity of the gas mixture of only 0.5-1%.

To compare the coefficients of thermal conductivity there must be, first, a heat source and, second, a heat-flux meter. In thermal-conductivity gas analyzers both these functions are fulfilled by identical devices called sensing elements. The sensing element in this case is an electrical resistor made of a material having a high

[1]Pseudobinary gas mixtures include those for which either 1) the coefficient of thermal conductivity does not depend on the concentration of the unmeasured components, or 2) the concentration of the unmeasured components is connected by a specific law with the concentration of the analyzed component.

temperature coefficient of electrical resistance (copper, nickel, platinum, tungsten) and heated by an electric current passing through it. With a change in the coefficient of thermal conductivity of the gas surrounding the sensing element, there is a change in the quantity of heat fed to the latter and, consequently, a change in its temperature, which leads to a change in the electrical resistance. Heat transfer from the heated sensing element is realized due to molecular thermal conductivity, convection heat transfer, radiation, and the thermal conductivity of the sensing element itself (so-called "end cooling"). To obtain high sensitivity, all forms of heat transfer except molecular thermal conductivity must be reduced to a minimum. This is done by special configuration of the sensing elements. In modern sensing elements of thermal-conductivity gas analyzers, the various types of heat transfer are approximately as follows: convection – 2%, radiation – 1%, end cooling – up to 30%.

Sensing elements are coupled into the circuit of a Wheatstone bridge or some other type of bridge, where the measurement of their electrical resistance is converted into a change of voltage or current in the measuring diagonal of the bridge.

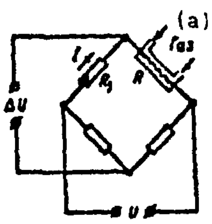

Fig. 2. Basic bridge circuit for a thermal-conductivity gas analyzer. KEY: (a) gas.

Disregarding heat losses due to radiation, convection, and end cooling, we can express the voltage on the measuring diagonal of an equal-arm bridge with one sensing element (Fig. 2) by the following formula [6]:

$$\Delta U = \frac{IRR_1R_0\alpha}{k(R+R_1)} \frac{\lambda_2-\lambda_1}{\lambda_2\lambda_1}, \qquad (5)$$

where I is the current passing through the sensing element; R and R_1 are the resistances of the sensing element and the contiguous arm of the bridge, respectively; R_0 is the resistance of the sensing element at 0°C; α is the temperature coefficient of electrical resistance of the sensing-element material; k is a coefficient which characterizes the geometric conditions of heat transfer; λ_1 and λ_2 are coefficients of thermal conductivity of a gas mixture without a measured component and with measured components, respectively.

For low concentrations of the measured component we can set $\lambda_1\lambda_2 \approx \lambda_l^2$, from which it follows that the voltage in the measuring diagonal of the bridge depends greatly on the coefficient of thermal conductivity of the background gas (i.e., the sum of the undefined components of the mixture). For example, 1% hydrogen in air has a higher sensitivity than 1% air in hydrogen. From formula (5) it follows that the readings of the gas analyzer depend on the current passing through the sensing element and on the temperature of the ambient medium, since the temperature of the ambient medium in turn stipulates the coefficients of thermal conductivity and the resistance of the sensing element. In order that changes of these factors not cause instrument errors, special measures are taken. The instrument readings theoretically should not depend on a change in pressure of the analyzed gas, since the thermal conductivities of gases do not depend on pressure within very broad limits. However, as was noted above, for the sensing elements there is a convective component of heat transfer which changes with a change in pressure. Due to this, the readings of the thermal-conductivity gas analyzers can depend to a certain extent on a change in pressure of the analyzed gas mixture.

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