MEASUREMENT OF THE HEAT OF MIXING OF MODERATELY DENSE GASES

Yu. I. Popov

UDC 546.49+533.1

We have measured the heat of mixing of the gaseous mixtures CO_2–H_2, CO_2–He, Ar–He, and N_2–He at constant volume, at pressures from 2 to 25 bar, temperature 295°K, and a 14.3% concentration of the heavy component. We have determined the excess enthalpy of these mixtures, which varies slowly with pressure.

The dependence of the excess caloric functions on pressure and on the concentration of miscible gases has not been adequately studied.

The published data on the measurement of the heat of mixing of moderately rarefied and moderately dense gases [1-3] showed that the excess enthalpy of gaseous mixtures varies slowly with pressure for moderately dense gases, and is practically independent of pressure for moderately rarefied gaseous mixtures. These data are at variance with statements of a number of authors (cf. bibliography in [3]) who measured the heat of mixing of gases in a continuous-flow calorimeter at pressures above 10-20 bar, and assumed that at lower pressures the excess enthalpy would be directly proportional to the pressure, as follows from the theory of second virial coefficients. In extrapolating the results of their measurements to lower pressures the authors of these papers assume that their measurements confirmed the correctness of the theory of virial coefficients. However, the only published data on a measurement of the heat of mixing of gases with a continuous-flow calorimeter at pressures below 2 bar [4, 5] show that the heat of mixing tends to zero with decreasing pressure even more rapidly than by a direct proportionality law. Thus, the technique of measuring the excess enthalpy of gases on a continuous-flow calorimeter in the pressure range of a few atmospheres is unacceptable because of large errors.

The present paper is a continuation of [2, 3] on the measurement of the heat of mixing of moderately dense gases in a closed calorimeter. The technique of making measurements with this calorimeter, its construction, and the method of calculating the excess enthalpy from the measured data are described in [2, 3]. The new calorimeter differs from the one used in [2, 3] only in the location of the internal diaphragm, which was placed so that the concentration of the heavy component fed into the lower part of the calorimeter was 14.3%.

The cooling of the bomb after the separating valve was opened reached a maximum in 1-3 min, depending on the pressure of the gas. The end of mixing was checked by the cessation of the pressure rise in the calorimeter. The mixing was practically complete in 1-3 min after the extremum of the temperature effect as a function of pressure was reached.

The excess enthalpy was calculated with the formula [3]

$$H^E \cong Q_{T,V} + pV^E,$$

where $Q_{T,V}$ is the isochoric heat of mixing, which was calculated from the change of temperature of three microthermistor transducers fastened to the wall of the calorimetric bomb. The correction pV^E, equal approximately to $V\Delta p$, does not exceed 10% (for the CO_2–He mixture at a pressure of 25 bar) of the total value of H^E in the measurement of the heat of mixing of gases of a given concentration. For a pressure of miscible gases below 10-15 bar, the correction becomes negligible in comparison with $Q_{T,V}$. In [2, 3] it was indicated that this correction for a pressure of a few bar can be neglected, and the excess enthalpy becomes nearly equal to the isochoric heat of mixing $Q_{T,V}$. Altunin et al. [4] point out the necessity of taking account of the correction pV^E even at low pressures. It is clear that taking account of this correction would lead us only to a very small increase of the values obtained for the excess enthalpy, and not to results one or two orders of magnitude smaller than those obtained by L. S. Kotousov [1].

V. I. Ul'yanov (Lenin) Electrotechnical Institute, Leningrad. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 42, No. 6, pp. 946-949, June, 1982. Original articles submitted March 18, 1981.

0022-0841/82/4206-0635$07.50

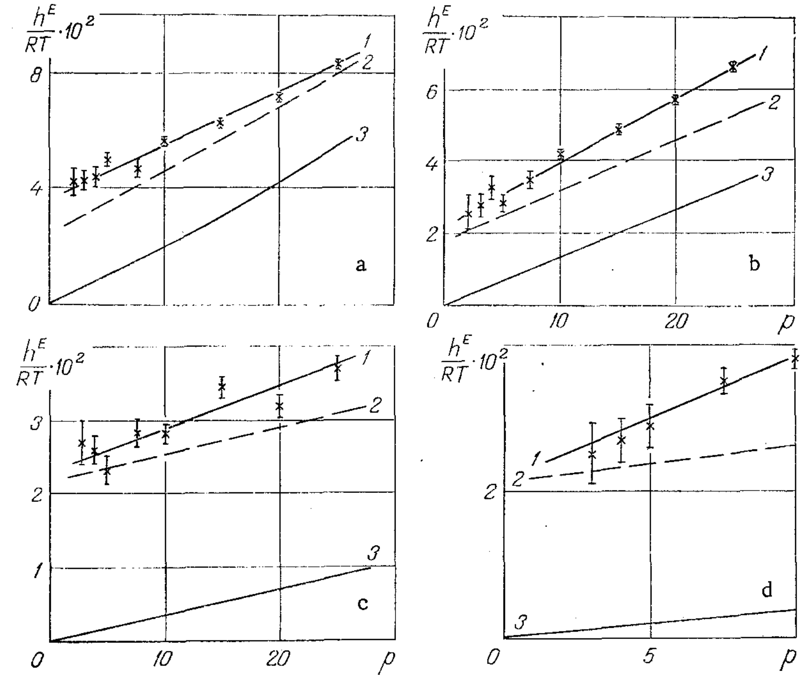

Fig. 1. Dependence of reduced excess enthalpy on pressure p (in atm) at a temperature of 295°K for a 14.3% mole fraction of the heavy component. Mixtures: a) CO_2—He; b) CO_2—H_2; c) N_2—He; d) Ar—He: 1) our measurements; 2) nonequilibrium thermodynamic calculation [6, 7]; 3) calculation based on the equation of state with second and third virial coefficients.

It was indicated in [4] that in free convection, which prevailed in the experiments in [1], the heat-transfer coefficient depends on the temperature drop between the calorimeter wall and the air thermostat. However, the assumption of a constant heat-transfer coefficient is reasonable for the following reasons. The measurable temperature drop is of the same order of magnitude as the temperature drop between different parts of the inner walls of the cell of the air thermostat in which the calorimeter was located. The linear dimensions of the inner cavity of this cell are an order of magnitude larger than those of the calorimeter. Therefore, the Grashof number and the corresponding thickness of the boundary layer at the air—calorimeter boundary are determined by the third power of the linear dimensions of the thermostat cavity, and not the calorimeter. This means that the heat-transfer coefficient in the experiment can be taken constant, independent of the magnitude of the temperature drop between the calorimeter and the thermostat, which is observed in the experiment.

In the present and earlier [2, 3] articles the heat-transfer coefficient, being a characteristic of the nonadiabaticity of the calorimeter, was taken into account by measuring the rate of decrease of the temperature effect of cooling of the calorimetric bomb. The computational procedure is described in [3]. The measurements with a 14.3% concentration of the heavy component the correction for the nonadiabaticity of the calorimeter was 15-20% of the maximum thermal effect recorded by the transducers. Earlier experiments [2, 3] showed that this correction was somewhat higher for equimolar mixtures.

We present below the results of the measurements of the excess enthalpy of the mixtures CO_2—H_2, CO_2—He, Ar—He, and N_2—He at a temperature of 295°K and a 14.3% mole fraction of the heavy component in the pressure range 2-25 bar.

High-purity gases were used in the experiments. The content of the principal material was 99.99% for helium, 99.7% for nitrogen, 99.99% for argon, and 98.8% for carbon dioxide. Electrolytically pure hydrogen was used.

At least 10 measurements were performed for each pair of gases at a given pressure above 5 bar, and at least 15-20 measurements at a given pressure in the range 2-5 bar.

Figure 1 shows the results of the determination of the excess enthalpy. These data were compared with the theoretical values obtained with the theory of virial coefficients, and with values calculated according to the phenomenological procedure [6, 7].

A comparison with data obtained with the continuous-flow calorimeter shows that for an Ar—He mixture at a pressure of 10 bar, the excess enthalpy is approximately three times as large as the excess enthalpy of this mixture at a pressure of 18.4 bar and a 0.26 mole fraction of Ar, according to data in [8].

NOTATION

p, pressure of gaseous mixture; Δp, change in pressure during mixing; V, volume of mixture; V^E, excess volume, $Q_{T,V}$, heat of mixing at constant volume and temperature; H^E, excess enthalpy; h^E, molar excess enthalpy; T, absolute temperature; R, universal gas constant.

LITERATURE CITED

1. L. S. Kotousov, "Measurement of the heat of mixing of simple moderately rarefied gases," Inzh.-Fiz. Zh., 39, No. 4, 1066-1069 (1980).
2. L. S. Kotousov, Yu. I. Popov, and A. N. Sviridov, "Measurement of the heat of mixing of Ar—He and N_2—He in the pressure range 2-15 bar," C. R. Acad. Sci., Paris, 287, Ser. B, 109-111 (1978).
3. Yu. I. Popov and L. S. Kotousov, "Measurement of the heat of mixing of moderately dense gases," Inzh.-Fiz. Zh., 39, No. 4, 1066-1069 (1980).
4. V. V. Altunin, V. F. Bondarenko, and D. O. Kuznetsov, "Heat of mixing of gases at low pressures," Teplofiz. Vys. Temp., 15, 216-218 (1977).
5. V. F. Bondarenko, "Experimental and theoretical study of caloric properties of compressed gaseous mixtures," Author's Abstract of Candidate's Dissertation, Moscow (1975).
6. L. S. Kotousov and A. N. Sviridov, "Calculation of excess potentials of binary mixtures of gases," Zh. Tekh. Fiz., 47, 1324-1332 (1977).
7. L. S. Kotousov, L. A. Mezrina, and Yu. I. Popov, "Calculation of excess potentials of binary mixtures of gases," Zh. Tekh. Fiz., 50, 1270-1274 (1980).
8. B. Van Eijnsbergen and J. J. M. Beenakker, "Measurements of the isobaric heat of mixing for gaseous mixtures CH_4—Ar, CH_4—N_2, H_2—CH_4, He—CH_4, and He—Ar between 170 and 293°K and at pressures up to 120 atm," Physica, 39, 499-518 (1968).

MEASUREMENT OF THERMOPHYSICAL PROPERTIES OF MIXTURES BY PERIODIC HEATING OF PROBES

S. N. Kravchun

UDC 536.223

We analyze the theory of the method of periodic heating of probes as applied to the study of thermophysical properties of liquid and gaseous mixtures.

One of the promising methods of investigating thermophysical properties of fluids is the method of the periodic heating of probes [1-4]. The gist of the method consists in the recording of temperature fluctuations of a probe (wire or metal foil) when heated by an alternating current. The amplitude and phase of the temperature fluctuations of the probe depend on the thermophysical properties of the fluid in which it is immersed (on the thermal conductivity λ and the volumetric heat capacity $c_p\rho$ for a cylindrical probe, and on the thermal activity $b = \sqrt{\lambda c_p \rho}$ for a plane probe). The measurement of the amplitude and phase of the temperature fluctuations of the probe by electronic means makes it possible to determine these thermophysical characteristics. The method developed can be used to study the thermophysical properties of pure gases and liquids over a wide range of states [1]. The application of the method of periodic heating to the investigation of solutions requires extension of the theory of the method.

It is well known that in gaseous and liquid mixtures a temperature gradient gives rise not only to a heat flux, but also to a diffusive flux (thermal diffusion, the Soret effect).

M. V. Lomonosov State University, Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 42, No. 6, pp. 949-955, June, 1982. Original article submitted March 3, 1981

0022-0841/82/4206-0637$07.50