MEASUREMENT OF THE MIXING TEMPERATURE OF MODERATELY DENSE GASES

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The mixing temperature was measured at constant volume with pressures of 2-25 bar and temperature of 294°K. The excess enthalpy of mixtures CO_2—He and N_2—He was determined; it was found in this region to be only weakly dependent on the pressure.

The mixing temperature with specified pressure and temperature, i.e., the excess enthalpy, has been studied very insufficiently in the past in regard to moderately rarefied and moderately dense gases. For dense gases it was determined in an isothermal flow calorimeter [1-9] at pressures of more than 10 or 20, sometimes 30 bar, and also in an adiabatic flow calorimeter [8, 9]. The flow-calorimeter method was used in verifying the correctness of the concept of the mixed second virial coefficient in calculating the mixing temperature of moderately rarefied gases [10].

The authors of the works above extrapolated the mixing temperatures on the basis of a direct proportional dependence on the pressure in the region of lower pressures in accordance with only the second virial coefficient in the equation of state of the mixtures being taken into account. Altunin et al. [10] measured the excess enthalpy of the mixtures Ar—He and CO_2—He in the regions 0.6-2 and 0.2-2 bar, respectively, at 295°K. And though the experimental data from a flow calorimeter for CO_2—He indicate an even greater drop of the mixing temperature than would correspond to direct proportionality, the authors of [10] concluded that the law of direct proportionality may be used.

The articles [11, 12] present the results of measurements of the excess enthalpy in a closed calorimeter for gases in the regions 0.15-0.9 and 2-15 bar, respectively. These data show that the excess enthalpy is only weakly dependent on the pressure in the range 0.15-15 bar. At pressures of a few bar or less it is much higher than the value calculated by the equation of state with the second virial coefficient, and this is particularly characteristic of mixtures of He and H_2 with heavier gases.

Below we present the results of measuring the excess enthalpy of the mixtures CO_2—He and N_2—He at 294°K, the mole fraction of the heavy component being 56% in the range 2-25 bar.

We used a thick-walled closed copper calorimeter whose design and dimensions, as well as the arrangement and method of measurements on it, were described in [12]. The principle of measurement consists in recording the changes in the temperature of three microthermistors STZ-18 glued to certain points of the calorimeter walls for finding the mean cooling effect of the bomb upon mixing of the gases originally filling its two parts and separated by a movable shutoff device. The nonuniform cooling of the calorimeter at the initial stage of mixing is caused by the non-steady-state diffusion thermoeffect, which, throughout the entire calorimeter and during the entire mixing time, also integrally gives rise to the effect of the mixing temperature (see [13]).

After the separating valve has been opened, the cooling of the bomb attains its maximum after 1-6 min, depending on the gas pressure. However, heat exchange with the environment then causes a gradual drop in the temperature effects. Checking the end of mixing was possible to carry out after the pressure ceased to change in this process, the changes being registered by a reference manometer class 0.6; the cessation of change in pressure was fairly noticeable at pressures exceeding 10 bar. Mixing practically ended at the instant following the attainment of the extremum of the temperature effect after 1-4 min, depending

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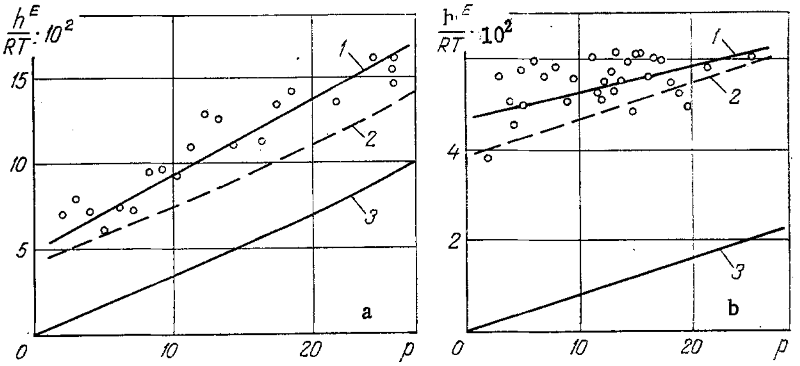

Fig. 1. Dependence of the reduced excess enthalpy on pressure at 294°K and mole fraction of the heavier component 56%. Mixture CO_2—He (a) and N_2—He (b): 1) our measurements; 2) nonequilibrium thermodynamic calculation [14]; 3) calculation by the equation of state with the second and third virial coefficients. p, bar.

on the pressure. From the course of the temperature effect, the rate of its drop due to heat exchange was determined. This rate was multiplied by the time from the beginning of mixing, and the given correction of the mixing temperature was taken into account in the final result according to the heat capacity of the calorimeter. The correction calculated according to the rate of drop of the effect at later instants was always somewhat lower, which indicates that the method of calculating it is correct.

In the given calorimeter, direct measurements yield the mixing temperature at constant volume and temperature. This last is correct because the temperature effects always satisfied the condition $\Delta T \ll T$. To go over to the excess enthalpy, we use the general thermodynamic relationship

$$\left(\frac{\partial U}{\partial x_1}\right)_{T,p} = \left(\frac{\partial U}{\partial x_1}\right)_{T,V} + \left(\frac{\partial U}{\partial V}\right)_{T,x_1} \left(\frac{\partial V}{\partial x_1}\right)_{T,p}. \tag{1}$$

If we integrate from $x_1 = 0$ to $x_1 = x_{1e}$ in one part of the calorimeter containing initially the pure gas 2, and correspondingly from $x_1 = 1$ to $x_1 = x_{1e}$ in the other part, we obtain

$$U(x_{1e}) - U_1^0 - U_2^0 = U(x_{1e}) - N\,(x_{1e}u_1^0 + x_{2e}u_2^0) = \Delta U. \tag{2}$$

Hence

$$U^E \equiv (\Delta U)_{T,p} = (\Delta U)_{T,V} + \left(\frac{\partial \bar{U}}{\partial V}\right)_{T,x_1} V^E = Q_{T,V} + \left(\frac{\partial \bar{U}}{\partial V}\right)_{T,x_1} V^E, \tag{3}$$

where $(\partial \bar{U}/\partial V)_{T,x_1}$ is the mean value according to the law of the mean. But

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_S + \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T = -p + T\left(\frac{\partial p}{\partial T}\right)_V. \tag{4}$$

It is obvious that

$$\delta p = -p + T\left(\frac{\partial p}{\partial T}\right)_V \ll p \tag{5}$$

with the given conditions of measurement.

Finally,

$$U^E = Q_{T,V} + \bar{\delta} p V^E, \tag{6}$$

and for excess enthalpy we have

$$H^E = Q_{T,V} + \bar{\delta} p V^E + pV^E \cong Q_{T,V} + pV^E. \tag{7}$$

The correction pU^E is negligibly small at pressures not exceeding a few bar according to the data for the magnitude of U^E. However, at pressures exceeding 5 or 10 bar, especially when the mixture CO_2—He is involved, this correction must not be neglected any more. In the first approximation

$$pV^E = V\Delta p. \quad (8)$$

Expression (7) was used in [11], and it was noted that for the investigated mixtures at pressures of the order of magnitude 1 bar or less, the excess internal energy and the excess enthalpy differ only negligibly little from each other.

Figure 1 shows the results of the determination of excess enthalpy. These data are compared with the theoretical values obtained by analysis of the equation of state with the second and third (for the mixture CO_2—He) virial coefficients, and also with the values calculated in accordance with the phenomenological approximation [14] at a pressure of about 1 bar with the addition of the integral $\Delta h^E(p) = \int_1^p \left(v^E - T\frac{\partial V^E}{\partial T}\right) dp$ for higher pressures.

A comparison with the data of [15] shows that at a pressure of 25 bar, our results are about one-half higher than the values of excess enthalpy obtained in [15] at a pressure exceeding 35 bar in the vicinity of this pressure. However, these data were obtained at 313°K. Previously [12], it had been discovered that our data at a pressure of about 20 bar and a temperature of 294°K for the mixture Ar—He are also higher than the results of [2].

NOTATION

T, absolute temperature; ΔT, change in the temperature of the calorimetric bomb; p, pressure of the mixture; Δp, change in pressure during mixing; V, volume of the mixture; V^E, excess volume; v^E, mole excess volume; U, internal energy of the mixture; $U^\circ_{1,2}$, internal energy of the pure gases 1 and 2, respectively; $u^\circ_{1,2}$, mole internal energy of the pure gases; $(\Delta U)_{T,V} = Q_{T,V}$, mixing temperature with constant volume and temperature; U^E, excess internal energy; H^E, excess enthalpy; h^E, mole excess enthalpy; R, universal gas constant; N, total number of moles of gases 1 and 2; x_1, mole fraction of gas 1; x_{1e}, equilibrium mole fraction after mixing.

LITERATURE CITED

1. M. Knoester, K. W. Taconis, and J. J. M. Beenakker, "Excess enthalpies of gaseous mixtures of hydrogen, nitrogen and argon between 150 and 293°K and pressures up to 130 atm," Physica, 33, 389-409 (1967).
2. 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).
3. J. I. Lee and A. E. Mather, "The excess enthalpy of gaseous mixtures of nitrogen and carbon dioxide," J. Chem. Thermod., 2, 881-895 (1970).
4. J. I. Lee and A. E. Mather, "Excess enthalpy of gaseous mixtures of nitrogen and carbon dioxide," J. Chem. Eng. Data, 17, 189-192 (1972).
5. J. I. Lee and A. E. Mather, "Excess enthalpy of gaseous mixtures of carbon dioxide with methane," Can. J. Chem. Eng., 50, 95-100 (1972).
6. A. V. Hejmadi, D. L. Katz, and J. E. Powers, "Experimental determination of the enthalpy of mixing $N_2 + CO_2$ under pressure," J. Chem. Thermod., 3, 483-496 (1971).
7. R. R. Klein, C. O. Bennett, and B. F. Dodge, "Experimental heats of mixing for gaseous nitrogen and methane," AIChE J., 17, 958-965 (1971).
8. V. V. Altunin, V. F. Bondarenko, and D. O. Kuznetsov, "Experimental investigation of the enthalpy of binary gas mixtures," Teplofiz. Vys. Temp., 11, 533-538 (1973).
9. V. V. Altunin, D. O. Kuznetsov, and V. F. Bondarenko, "Experimental investigation of the thermodynamic properties of binary gas mixtures," Teplofiz. Vys. Temp., 12, 513-518 (1974).
10. V. V. Altunin, V. F. Bondarenko, and D. O. Kuznetsov, "Mixing temperature of gases at low pressures," Teplofiz. Vys. Temp., 15, 216-218 (1977).
11. L. S. Kotousov, "Measurement of the mixing temperature of simple, moderately rarefied gases," Zh. Fiz. Khim., 46, 863-866 (1972).

12. L. S. Kotousov, Y. I. Popov, and A. N. Sviridov, "Mesure de la chaleur de mélange de Ar—He et N_2—He dans le domaine de pression: 2-15 bar," C. R. Acad. Sci. Paris, 287, Ser. B, 109-111 (1978).
13. L. S. Kotousov, "Determination of the thermodynamic mixing potential of a binary mixture on the basis of an analysis of the processes in interdiffusion," Zh. Tekh. Fiz., 40, 1994-2004 (1970).
14. L. S. Kotousov and A. N. Sviridov, "Calculation of the excess potentials of binary gas mixtures," Zh. Tekh. Fiz., 47, 1324-1332 (1977).
15. V. F. Bondarenko, "Experimental and theoretical investigation of the caloric properties of compressed gas mixtures," Author's Abstract of PhD Thesis, MÉI, Moscow (1975).

ANALYSIS AND CORRELATION OF NEW DATA ON THE THERMOPHYSICAL PROPERTIES OF MERCURY VAPOR

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The article contains a critical analysis of the experimental data concerning the thermophysical properties of mercury vapor and the coordination on the basis of the simultaneous processing of the data on saturation pressure, viscosity, and heat conductivity.

In the preparation of reference data on the thermophysical properties of mercury vapors for the monograph [1], the properties at temperatures up to 2000°K and pressures of 10 MPa were generalized on the basis of a single potential of interatomic interaction of atoms, chiefly in the 6^1S_0 state. We implemented the method of simultaneous determination of the sublimation temperature ΔH_0^0 and two parameters of the selected potential: the potential well depth ε and the collision diameter d with joint approximation of the experimental data on the saturation pressures P_S–T_S, and also viscosity $\eta(T)$ and heat conductivity $\lambda(T)$ of the rarefied vapor. The main calculations of the reference data were carried out with the aid of the Morse potential ($\beta = 4.5$), and later [2], the Lennard-Jones (L.-J.) potential (9-6) was also successfully applied.

At the same time, the following problems in the investigation of the properties of mercury were discovered.

1. The experimental data on the heat capacity of the solid phase at 4-20°K contain a considerable error, making the principal contribution to the error in determining the sublimation temperature $\Delta(\Delta H_0^0) = 60$ J/mole, and they are, as noted in [2], probably exaggeratedly high.

2. On the basis of a critical analysis of the data on the viscosity and heat conductivity of the vapor, preference was given to the results of Braune, Basch, and Wentzel [3] regarding viscosity in the interval 490-880°K, and this work was the basis for determining the potential. Like any single work, it needed confirmation.

3. In joint processing of the data, it was dicovered [1, 2] that the only results of measuring saturation pressure in the interval 600-800°C [4] claiming very good accuracy were in effect 1.5-2% too high.

At present we are in possession of the results of new measurements of the properties of mercury vapor which, on the whole, confirmed the earlier generalizations [1, 2]. Part of this work [5, 6] was carried out upon the initiative of the Section of Liquid Metals, Scientific Council "Thermophysics" of the Academy of Sciences of the USSR with the object of verifying existing data. Then we give a brief analysis of the new experimental data, a selection of the errors for calculating the weights, an algorithm for and the results of repeated joint processing.

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