Speed of sound in gas solution of R-134a / R-227ea refrigerants

S G Komarov and S V Stankus
Kutateladze Institute of Thermophysics SB RAS, Novosibirsk, Russia

E-mail: stankus@itp.nsc.ru

Abstract. The speed of sound of the gaseous mixture of R-134a and R-227ea (30.73 / 69.27 mass.%) was investigated by an ultrasonic interferometer over the temperature range of 293–373 K and at pressures from 0.12 MPa up to 1.3 MPa. The measurement errors for the temperature, pressure, and speed of sound were estimated at 20 mK, 4 kPa, and 0.1–0.3%, respectively. The approximation dependences for the speed of sound in the vapor were obtained and their errors were estimated. The obtained data were compared with the results of calculations by the REFPROP software.

1. Introduction
R-134a and R-227ea refrigerants have zero ozone depletion potential, so their mixtures have prospects for the use in various refrigeration devices. Currently, one blend of this system (R-423a refrigerant) has been widely used as a substitute for ozone-hazardous refrigerant R-12 in centrifugal chillers. The thermodynamic description of refrigerants, including mixed ones, is based on the definition of Helmholtz free energy [1]. The most sensitive property for its approbation is the speed of sound ($U$).

To determine possible errors in the evaluation of the thermal properties of mixed refrigerants based on the system R-134a / R-227ea by the widely used REFPROP program [2], we measured $U$ for the mixture of 30.7% R-134a / 69.3% R-227ea in the vapor phase and on the dew line.

2. Experiments
The speed of sound was measured by the variable base ultrasonic interferometer method. The operating frequency was about 1 MHz. In the range of state parameters studied, no $U$ dispersion was observed. All parts of the setups were made of stainless steel. The cell was immersed into a fluid thermostat. The temperature in the bath was held at 5 mK throughout the measurements. The temperature ($T$) was measured with PTS-10 first class reference resistance thermometers, calibrated in the Siberian R&D Institute of Metrology, with the error within 0.02°C. The pressure ($p$) was measured with a quartz manometer preliminarily calibrated against a deadweight gage. A membrane zero-indicator made of stainless steel was used. The uncertainty of the pressure measuring was no more than 4 kPa. A detailed description of the experimental technique and setup was given in the previous paper [3]. To estimate the instrumental error, we measured the speed of sound in pure argon. The results obtained during these experiments differ from the most reliable data by no more than 0.06%.
3. Results

The gas mixture had a composition of 30.73 mass.% R-134a and 69.27 mass.% R-227ea. It was prepared by the weight method. The used refrigerants were R-227ea with a purity of 99.99% produced by the “Prikладная Химия” (Applied Chemistry) Russian Research Center, and R-134a with a purity of 99.9% produced by Forane, France.

The speed of sound in the blend was measured along five isotherms with a 20 K increment from 293 K, with the estimated error within 0.1-0.3% [3]. The results of the experiments with R-134a / R-227ea mixture are given in tables 1, 2 and figure 1.

Table 1. The experimental speed of sound of R-134a / R-227ea mixture.

| T (K)  | p (MPa) | U (m/s) | T (K)  | p (MPa) | U (m/s) |
|--------|---------|---------|--------|---------|---------|
| 293.15 | 0.1234  | 133.20  | 333.15 | 1.0677  | 120.11  |
| 293.15 | 0.2197  | 129.84  | 353.15 | 0.1493  | 146.92  |
| 293.15 | 0.3877  | 124.30  | 353.15 | 0.2700  | 144.54  |
| 313.15 | 0.1317  | 137.67  | 353.15 | 0.4890  | 140.95  |
| 313.15 | 0.2372  | 135.19  | 353.15 | 0.7487  | 136.10  |
| 313.15 | 0.4219  | 130.08  | 353.15 | 0.9940  | 131.14  |
| 313.15 | 0.6347  | 123.72  | 353.15 | 1.1190  | 128.49  |
| 313.15 | 0.8350  | 117.85  | 353.15 | 1.1728  | 127.29  |
| 323.15 | 0.9713  | 117.52  | 373.15 | 0.1586  | 150.91  |
| 323.15 | 1.0123  | 116.09  | 373.15 | 0.2864  | 148.72  |
| 333.15 | 0.1406  | 142.32  | 373.15 | 0.5201  | 145.68  |
| 333.15 | 0.1407  | 142.25  | 373.15 | 0.8032  | 141.40  |
| 333.15 | 0.2534  | 139.61  | 373.15 | 1.0744  | 137.15  |
| 333.15 | 0.4553  | 135.74  | 373.15 | 1.2119  | 134.83  |
| 333.15 | 0.6923  | 130.10  | 373.15 | 1.2127  | 134.82  |
| 333.15 | 0.9130  | 124.51  | 373.15 | 1.2714  | 133.81  |
| 333.15 | 1.0220  | 121.46  | 373.15 | 1.2719  | 133.84  |

Experimental data on the speed of sound on isotherms $U(p)$ were approximated polynomial functions of pressure:

$$U(p) = A_0 + A_1 p + A_2 p^2$$

(1)

The coefficients of the polynomials are given in table 3. The mean square deviations of the measured values from the approximating dependences $U(p)$ were 0.045% (figure 2).

Table 2. The experimental speed of sound of R-134a / R-227ea mixture on the dew line.

| T (K)  | p (MPa) | U (m/s) | T (K)  | p (MPa) | U (m/s) |
|--------|---------|---------|--------|---------|---------|
| 293.15 | 0.4677  | 121.97  | 303.15 | 0.6355  | 120.45  |
| 293.15 | 0.4712  | 122.68  | 303.15 | 0.6377  | 120.51  |
| 293.15 | 0.4738  | 122.83  | 313.15 | 0.8273  | 117.12  |
| 303.15 | 0.6341  | 120.17  | 313.15 | 0.8370  | 117.17  |
| 303.15 | 0.6345  | 120.62  | -      | -       | -       |
Figure 1. Experimental isotherms for the speed of sound in 30.7% R-134a / 69.3% R-227ea refrigerant vapor at (1) 293.15, (2) 313.15, (3) 333.15, (4) 353.15, and (5) 373.15 K.

Using the obtained data on the speed of sound in the vapor and the known thermodynamic equation:

$$C_p^0(T) = \frac{R}{1 - \frac{RT}{\mu U_0^2}}$$

one can easily obtain the ideal-gas heat capacity for the refrigerants. In the equation (2), $T$ is the temperature in K, $R = 8.314472$ J/(mole K) is the universal gas constant, $U_0(T)$ is the speed of sound at zero pressure, and $\mu$ is the molecular mass (0.141126 kg/mol) for 30.73 mass.% R-134a and 69.27 mass.% R-227ea mixture. In contrast to the speed of sound the ideal-gas heat capacity of mixed refrigerants is a strictly additive value. Temperature dependences $C_p^0(T)$ of R-134a and R-227ea refrigerants included in the mixture were studied with sufficient reliability [2]. This, in particular, allows controlling the systematic errors in $U$ with the help of ideal-gas heat capacity of mixed refrigerants, because their heat capacity can be calculated from heat capacities of pure components by the laws for ideal solutions. Our calculations show that the deviations of our data on $C_p^0(T)$ from reference data in the interval 313-373 K lie in the range of 1.3–3.5%. Since the error of $C_p^0(T)$ in equation (2) for the given refrigerant composition approximately 22–30 times exceeds the error in $U$ measurement, then, for the speed of sound the discrepancy is 0.04–0.16%. This value lies within the estimated errors, which indicates the correctness of their evaluation.

Comparison with the values of speed of sound in the vapor phase for the mixture of 30.73 mass.% R-134a and 69.27 mass.% R-227ea calculated from the fundamental state equation for Helmholtz free energy [2] shows that the deviations from our data do not exceed the total measurement error (mean absolute deviation is 0.09%). This indicates that the state equation obtained in [2] reliably describes thermodynamic properties of the R-134a / R-227ea refrigerant system in a wide range of state parameters.
**Table 3.** Coefficient in equation (1).

| Isotherm (K) | p interval (MPa) | $A_0$ (ms$^{-1}$) | $A_1$ (ms$^{-1}$MPa$^{-1}$) | $A_2$ (ms$^{-1}$MPa$^{-2}$) |
|-------------|------------------|-------------------|-----------------------------|-----------------------------|
| 293.15      | 0.12-0.39        | 137.30            | 33.596                      | 0.000                       |
| 313.15      | 0.13-0.84        | 141.08            | 24.511                      | 4.072                       |
| 333.15      | 0.14-1.07        | 144.89            | 17.844                      | 4.988                       |
| 353.15      | 0.15-1.17        | 149.32            | 15.800                      | 2.525                       |
| 373.15      | 0.16-1.27        | 153.07            | 13.484                      | 1.289                       |

**Figure 2.** Relative deviations of the experimental values of speed of sound in 30.7% R-134a / 69.3% R-227ea refrigerant vapor from the approximation (1) at (1) 293.15, (2) 313.15, (3) 333.15, (4) 353.15, and (5) 373.15 K.

4. Conclusions

New experimental data have been obtained on the speed of sound in vapors of R-134a and R-227ea refrigerants mixture, and ideal-gas heat capacities have been calculated in the temperature range of 293–373 K. Comparison of the obtained results with published data confirms the declared accuracy of the measurements and shows that the fundamental state equation for Helmholtz free energy used in the REFPROP database (version 8.0) allows one to calculate the speed of sound in vapor phase of R-134a / R-227ea system with a high accuracy.

**References**

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