S. G. Komarov, A. N. Solov'ev, and E. P. Sheludyakov

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We have examined the acoustic dispersion for $CFCl_3$ (freon-11), $CHFCl_2$ (freon-21), and $C_2H_3F_2Cl$ (freon-142), and also the absorption of ultrasound. All the freons were subjected to chromatography. No impurities were found in the freon-11; the freon-21 contained 0.019% water and 0.0041% insoluble residue, while the freon-142 contained 0.3% of freon-141, freon-143, freon-153, and other impurities.

Dispersion has previously been reported [1,2] for freon-11 and freon-21. The measurements were made at 373° K and pressures from 0.25 to 2.5 bar. Freon-142 has not been examined. To examine the effects of state parameters we substantially extended the temperature and pressure ranges.

The apparatus previously described [3] was used to examine the dispersion by ultrasonic interferometry at $2.2 \cdot 10^5$ and $2.1 \cdot 10^6$ Hz, along along nine isotherms for freon-11, ten for freon-21, and five for freon-142 at 293-433° K and 0.04-25 bar. A low-frequency apparatus [4] was also used with these isotherms to measure the speed of sound at 1 to 3 kHz. These velocities c may be considered as thermodynamic, i.e., independent of frequency. The excess velocity at high frequencies was determined relative to these values. Figure 1 shows c in m/sec as a function of pressure p (bar) for the 294.66, 333.16, 373.16, and 418.16° K isotherms for freon-11 at three frequencies: curves 1-3 correspond to $2.1 \cdot 10^6$, $2.2 \cdot 10^5$, and 10^3 Hz, respectively. S being the saturation curve. Freon-21 gave analogous curves.

The error in c at $2.1 \cdot 10^6$ Hz increased as p was reduced on account of deterioration in interferometer reaction and was 2-3% at the ends of the isotherms, so the error in the dispersion in this region was 10-20%. As p is raised (along an isotherm), the dispersion falls towards the values corresponding to the saturation curve. The lower isotherms showed a tendency to produce a minimum before the saturation curve was reached. The obvious dispersion region in freon-11 extended up to 14 bar (24 bar for freon-21), whereas freon-142 had dispersion only up to 0.3 bar, and the dispersion at low pressures was comparable with the error of measurement.

Figure 2 shows c as a function of T at 0.1 bar for freon-21 at 10^3 and 2.1 $\cdot 10^6$ Hz. The dispersion increases with T, which is due to increase in the thermal capacity of the internal degrees of freedom of the molecule. The results on the dispersion were used to calculate the specific heats of the internal and external degrees of freedom (the dis-





| γ lg (f / p) | ү lg (j / p) | γ 1g (f / p) | | |
|---|--|--|--|--|
| $\begin{array}{r} 292.76\\ 33.0 & 7.308\\ 38.0 & 7.208\\ 39.5 & 7.158\\ 27.5 & 6.908\\ 13.2 & 6.508\\ 6.5 & 6.158\end{array}$ | $\begin{array}{r} 373.16\\ 26.0 6.778\\ 27.3 6.738\\ 17.0 6.508\\ 6.5 6.000\\ 2.5 5.508\end{array}$ | $\left \begin{array}{c} 421.46\\ 18.0 & 6.308\\ 8.0 & 6.108\\ 3.0 & 5.508\\ 1.8 & 5.158\end{array}\right $ | | |

persion curves were idealized first). The results for c at 1 kHz were used in allowance for the deviation from ideal behavior without resort to theoretical calculations. The velocity of sound on the idealized dispersion curve was deduced by adding to the velocity measured at 2.1 MHz the difference between c in the ideal-gas state and c at 1 kHz. The thermal capacity $C_{V\alpha}$ of the external degrees of freedom was calculated from

$C_{\infty} = \sqrt{gRT \left(1 + R/C_{va}\right)},$

which is derived in relaxation theory [5], in which C_{∞} is the maximum value of c on the idealized dispersion curve. The thermal capacity C_{vi} of the internal degrees of freedom was calculated from

$$C_{vi} = C_v - C_{va}.$$

The quantity C_v was deduced from the known C_p^0 [6]. The following results are in kJ/mole-deg:

| $T^{\circ} \mathrm{K} = 3$ | 00 3 | 40 3 | 880 | 420 |
|----------------------------|-------|-------|------------|----------|
| $C_{vi} = 49.0$ | 53.1 | 57.0 | ·· <u></u> | Freon 11 |
| $C_{vi} = 36.4$ | 40.2 | 44.0 | 47,3 | Freon 21 |
| $C_{va} = 20.92$ | 20.92 | 20.92 | | Freon 11 |
| $C_{ra} = 16.76$ | 16.76 | 16.76 | 16.76 | Freon-21 |

These $C_{\rm Vi}$ differ from those of [2] by 20%, which is within the error of the measurements. We also measured the amplitude absorption coefficient for the saturated and superheated vapors of the three compounds:

$$\gamma = \frac{2.3}{x} \lg \frac{A_0}{A}$$



in which A_0 is initial amplitude, A is final amplitude, and x is distance in cm. The table gives the results for γ (in cm⁻¹) for three temperatures, where f is in Hz and p is in bar, for the saturated vapors. Figure 3 shows that γ falls as T (and hence p) increases. Freon-11 has the strongest absorption and freon-142 the least.

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