

weight hydrocarbons has been determined at six temperatures ranging from 100°F to 275°F and at pressures ranging from 15 to 50 000 psi by use of a rolling-ball viscometer. For three of the hydrocarbons for which pressure-density data were not available, the density was determined over the same limits of pressure and temperature by use of a flexible bellows piezometer. The group varies in molecular weight from 240 to 429 and comprises several structural families of chain to ring and cyclohexyl to benzenoid ring structure. When the pressure-viscosity data are plotted in the form  $\log \eta/d$  vs  $[(v_0/v)^4 - K(v_0/v)^2]$ , where  $\eta$  is the viscosity at pressure  $P$ ,  $v_0$  is the specific volume at atmospheric pressure,  $v$  is the specific volume at  $P$ , and  $K$  is a constant chosen for each compound, it is found that reasonably good straight lines are obtained.

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**LA4. A Study of the Compressions of Several High Molecular Weight Hydrocarbons.**\* W. G. CUTLER, R. W. SCHIESSLER, AND W. WEBB, *The Pennsylvania State University*.—Using the Bridgman siphon bellows technique, compressions for several very pure liquid hydrocarbons have been measured to pressures as high as 150 000 psi at 100°F, 140°F, 175°F, 210°F, 239°F, and 275°F. The hydrocarbons have a molecular weight range of 170 to 351 and include normal paraffins, cycloparaffins, fused ring aromatics, and fused ring naphthenes. The Tait equation,  $v_0 - v = C \log(1 + P/B)$ , provided a good empirical fit for the isotherms. In the above equation  $C$  and  $B$  are constants,  $v$  is the specific volume at pressure  $P$ , and  $v_0$  is the specific volume at atmospheric pressure. The Hudeleston relation,  $\log[v^3 P / (v_0^3 - v^3)] = a - b(v_0^3 - v^3)$ , where  $a$  and  $b$  are constants and other symbols have the same meaning as above, has also been examined. Isobars and isochores have been drawn and studied over the full range of pressure and temperature. The effect of molecular structure on the compressibility of the hydrocarbons has been examined.

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**LA5. Statistical Mechanics of Isotopic Systems with Small Quantum Corrections.**\* JACOB BIGELEISEN, *Brookhaven National Laboratory*.—The differences in the thermodynamic properties of isotopic molecules, which can be described by the first quantum correction ( $u^2/24$  law), depend on the difference in the reciprocal masses of the atoms in the molecule, and are, therefore, independent of all masses except for those atoms isotopically substituted. This theorem provides a rigorous proof of the rule of the geometric mean for gaseous molecules. The theorem shows that the partition function ratio for double labelled molecules is equal to the appropriate ratio for single labelled molecules. The rule of the geometric mean for the vapor pressures can be derived using the assumption that the internal energy states are the same in the liquid and gas. The vapor pressures of the liquid hydrogens can be calculated in good agreement with experiment from the vapor pressures of any two, e.g.,  $H_2$  and  $HD$ . The partition function ratios for molecules of the type  $XY_n$ ,  $XY_{n-1}Y'$  can be expressed in terms of the masses  $Y$  and  $Y'$  and the symmetrical stretching frequency. This permits an evaluation of the experimental data on the fractionation of  $H_2O^{16}$  and  $H_2O^{18}$  by cations in terms of the breathing frequency. The results are in agreement with predictions from an electrostatic model.

\* Research carried out under the auspices of the U. S. Atomic Energy Commission.

**LA6. Derivation of a Quantum-Statistical Transport Equation for Dilute Gases.** A. W. SÁENZ, *Naval Research Laboratory*.—We have derived a quantum-statistical transport equation for dilute gases composed of particles of spin zero using the

properties of Wigner distribution functions (d.f.'s), Kirkwood's method of time averaging over a suitable interval  $\tau$ ,<sup>1</sup> and the formal time-dependent scattering theory. Our main assumptions may be stated roughly as follows: (i) the hypothesis of binary collisions; (ii) the effect of the statistics need only be taken into account for pairs; (iii) the d.f.'s are slowly varying over suitable microscopic regions and the time-averaged d.f.'s depend only secularly on time; (iv) an assumption of molecular chaos appropriate to bosons. The collision terms of our equation of transport contain an exact cross section: they reduce to those given by Kirkwood and Ross<sup>2</sup> when we evaluate this cross section according to the first Born approximation. The relation of our work to that of Mori and Ono,<sup>3</sup> Ono,<sup>4</sup> and Kirkwood and Ross<sup>2</sup> will be mentioned.

<sup>1</sup> J. G. Kirkwood, *J. Chem. Phys.* 14, 180 (1946); 15, 72 (1947).

<sup>2</sup> J. G. Kirkwood and J. Ross, *J. Chem. Phys.* 22, 1094 (1954).

<sup>3</sup> H. Mori and S. Ono, *Progr. Theoret. Phys.* 8, 327 (1952).

<sup>4</sup> S. Ono, *Progr. Theoret. Phys.* 12, 113 (1954).

**LA7. Einstein-Bose Gas Below the Critical Temperature.** J. FORD AND T. H. BERLIN, *Johns Hopkins University*.—The canonical partition function for an ideal Einstein-Bose gas is often expressed as a contour integral and then evaluated by the method of steepest descent. It had previously been thought that this method failed below the critical temperature, since the saddle point then became congruent with a singularity of the integrand. This difficulty can be overcome by using an indented contour. The partition function thus evaluated yields the same expressions for thermodynamic variables as are obtained by other procedures.

**LA8. Statistical Mechanical Calculation of the Data of State of the Helium Isotopes at Intermediate Temperatures and Densities.**\* ABRAHAM S. FRIEDMAN AND IRWIN OPPENHEIM, *National Bureau of Standards*.—Series expansions for the quantum mechanical partition functions, distribution functions, and thermodynamic functions, which were developed previously,<sup>1</sup> have been applied to the computation of the quantum mechanical compressibility factors for the isotopes of helium. DeBoer's quantum corrected values of the Lennard-Jones 6-12 intermolecular force constants were used, and the differences in compressibility factors,  $Z_{He^4} - Z_{He^3}$  and  $Z_{He^4} - Z_{He^6}$  were computed over a wide temperature and pressure range.

\* Supported in part by the U. S. Atomic Energy Commission, Division of Research.

<sup>1</sup> I. Oppenheim, *Bull. Am. Phys. Soc.* 29, No. 8, 10 (1954), abstract D6.

**LA9. Ideal Gas Thermodynamic Functions of the Isotopic Hydrogen Sulfides.**\* LESTER HAAR, JOE C. BRADLEY, AND ABRAHAM S. FRIEDMAN, *National Bureau of Standards*.—The ideal gas thermodynamic functions for  $H_2S$ ,  $D_2S$ ,  $T_2S$ ,  $HDS$ ,  $HTS$ , and  $DTS$  were calculated from molecular data. The recent spectroscopic data for  $H_2S$  and  $D_2S$  by Allen<sup>1</sup> were employed. The zero-order frequencies and the moments of inertia of the other isotopes were calculated from the  $H_2S$  and  $D_2S$  data. The partition functions are obtained in closed form. The calculations include high-temperature corrections for vibrational anharmonicity, rotation-vibration coupling, centrifugal stretching, and a low-temperature correction for non-classical rotation, in addition to a correction for the ortho-para effect.<sup>2</sup> The statistical calculations were performed on the National Bureau of Standards digital computer—SEAC. Tables of  $C_p^0/R$ ,  $(H^0 - E_0^0)/RT$ ,  $-(F^0 - E_0^0)/RT$ , and  $S^0/R$ , have been calculated at close temperature intervals from 50°–5000°K.

\* Supported in part by the U. S. Atomic Energy Commission, Division of Research.

<sup>1</sup> H. C. Allen, Jr. (private communication).

<sup>2</sup> H. W. Woolley (in preparation).

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