A New Ab Initio Interaction Potential for CO-CO and the Calculation of Some Selected Thermophysical Properties

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A four-dimensional intermolecular potential energy hypersurface for two rigid carbon monoxide molecules has been determined using ab initio methods. A total of 1457 energy points have been calculated with the supermolecular approach at the CCSD(T) level, including the full counterpoise correction and an extrapolation to the complete basis set limit. A 128-parameter site-site potential function with seven sites per CO molecule has been fitted to the calculated energy points.

The new potential function has been tested by computation of the classical second pressure virial coefficient and its first-order quantum corrections. The most reliable experimental data are described within ± 1 $cm^3 \cdot mol^{-1}$ over a wide temperature range. Larger deviations occur only at the lowest temperatures, where the second pressure virial coefficient should be computed fully quantum mechanically.

Shear viscosity and thermal conductivity in the limit of zero density have been calculated based on the kinetic theory of molecular gases considering the second-order approximations. The generalized cross sections needed were evaluated by means of classical scattering trajectories employing the new potential function. The thermal conductivity cross sections were carefully corrected for vibrational degrees of freedom. The agreement with experimental data at room temperature is very good (within ± 1 %) for both shear viscosity and thermal conductivity. The new potential function allows reliable calculations of these properties even at very high temperatures, where experimental techniques are not easy to apply.