Fugacities of N_2, CO_2 and CH_4 in N_2-CO_2-CH_4 mixtures from 10-500 bars determined by Raman spectroscopy

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Fugacity represents the effective partial pressure of a component that takes into account the non-ideality of the component. The non-ideality is represented by the dimensionless quantitiy known as the fugacity coefficient, which is equal to unity for an ideal gas (i.e. the fugacity and the partial pressure of the component are equal), and deviates from unity in proportion to the degree of non-ideality of the component. In practice, determining the fugacity of a gas experimentally requires measuring the volumetric properties of the gas at various PTX conditions and deriving an EOS describing the volume (density) of the gas as a function of PTX, a process that can prove to be arduous as a single measurement of the volume at a given PTX condition is not sufficient. Recently, Lamadrid et al. [1] described a method to determine fugacity of gases in mixtures utilizing the pressure dependence of Raman bands of individual gas components. This study extends this method to determine fugacities of N_2, CO_2, and CH_4 for gas mixtures of 25% N_2, 25% CO_2, and 50% CH_4 and 15% N_2, 60% CO_2, and 25% CH_4.

Raman spectra were collected from 10-500 bars at 25°C. The peak positions for each of the individual gases were determined and calibrated using Ne lines. The partial pressures of the individual components calculated from the peak positions do not correspond to partial pressures determined form the relationship between mole fraction and total pressure, nor do the summation of the partial pressures equal the total pressure exerted on the gas mixture, indicating that the gases do not mix ideally. Fugacities determined for the individual components are in good agreement with fugacities calculated using the Redlich-Kwong EOS. The Raman-based method thus offers a relatively simple means to determine gas fugacities over a range of PTX conditions.

[1] Lamadrid et al., (2017) *J. Raman Spectroc.* **49**, 1-13.