

Comparison of gravimetric carbon dioxide compressibility data with four cubic equations of state

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Introduction

Gravimetric analysis provides direct measurement of gas phase and sample density given that they both contribute the upthrust due to buoyancy (Archimedes' Law). This force must be adequately corrected in order to convert weight readings to mass uptake in gravimetric sorption experiments. The contribution of gas compressibility to this correction can be significant depending on the species and operating conditions. The present study is intended to verify whether any of four cubic equations of state are suitable models for carbon dioxide at pressures to 10 bars and a temperature range between $-5\text{ }^{\circ}\text{C}$ and $30\text{ }^{\circ}\text{C}$.

Experimental method

The IGA-001 instrument was used as a gas densitometer to measure the buoyancy of an inert quartz float at controlled pressure and temperature. The volume of the float by helium displacement is $2.0 \pm 0.005\text{ cm}^3$.



Figure 1: The IGA gravimetric analyser

The IGA UHV chamber was evacuated to $<10^{-6}$ mbar initially and the float temperature regulated by a refrigerated re-circulating water bath within $\pm 0.05\text{ }^{\circ}\text{C}$. Carbon dioxide (BOC CP grade with molecular sieve filter) was introduced at equal steps (0.33 bar) and the entire sequence of isotherms at $5\text{ }^{\circ}\text{C}$ intervals was recorded automatically.

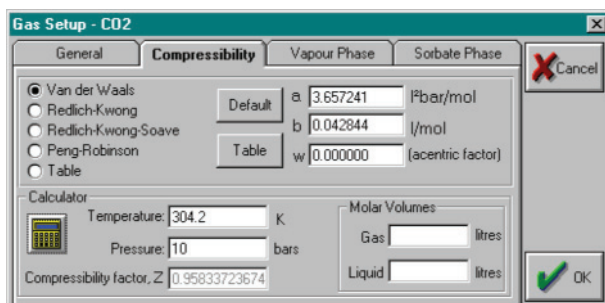


Figure 2: Gas Compressibility Menu in IGASwin software

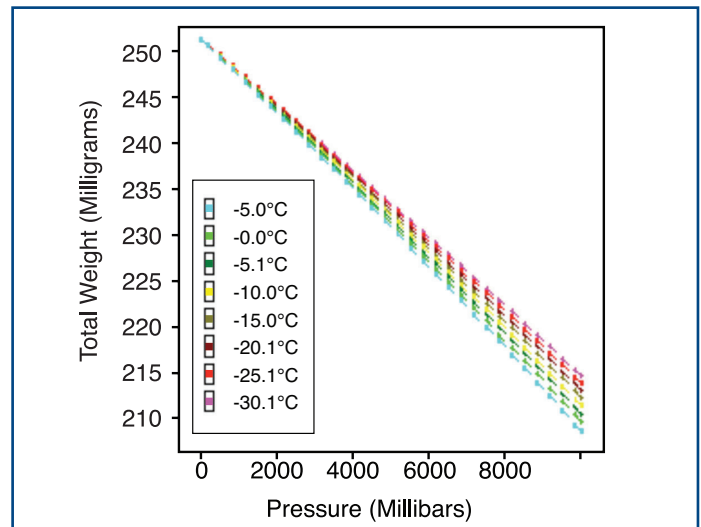


Figure 3: Apparent weight variation of quartz float as function of pressure and temperature in CO_2

Results

Isotherms of the measured force as a function of temperature and pressure are shown in Fig. 3. The weight trend will be linear for an ideal gas at constant temperature and deviations from linearity are due to compressibility, $Z(P,T)$. This linear (ideal gas) component is removed in Fig. 4 and corrections are clearly large compared with the measurement accuracy.

The correction for compressibility is then applied using four cubic equations of state (Figs. 5-8) as defined in the appendix. The critical temperature and pressure values used are from "The Properties of Gases and Liquids, 3rd Edition", by Reid, Prausnitz and Sherwood, McGraw Hill, 1977.

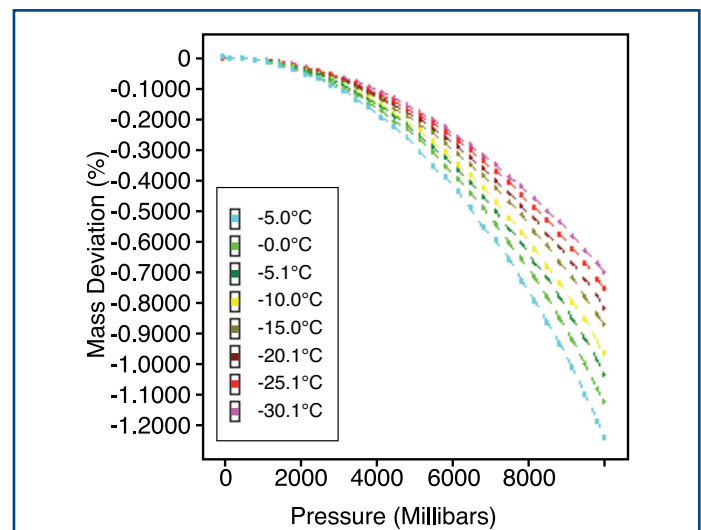


Figure 4: CO_2 compressibility expressed as deviation of calculated sample mass using the ideal gas law

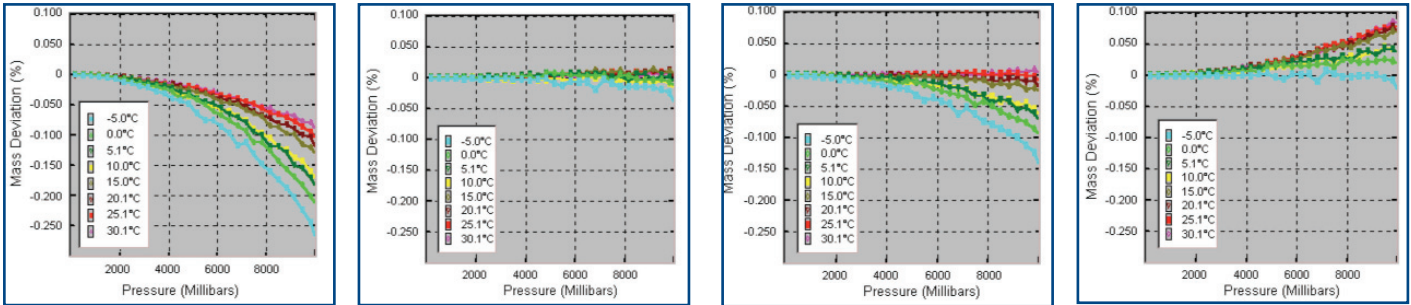


Figure 5, 6, 7 and 8: Data corrected for buoyancy using the VdW, RK, RKS, and PR models respectively.

The Redlich-Kwong (RK) model (Fig. 6) clearly shows the best overall compensation across these operating conditions. Compensation up to 5 bars operating pressure is within the measurement error and only the correction at sub-zero temperature contributes significant error at higher carbon dioxide pressure.

Conclusions

The IGA-001 instrument can be used to directly generate high-resolution compressibility data. In the present study a comparison with four cubic equations of state incorporated within IGA system software show that the RK model is the most suitable though still does not provide correction within the measurement accuracy. Alternatively the measured data can be used to generate a lookup table for interpolation of $Z(P, T)$. This is the most consistent method given the accuracy of corrections required for IGA mass sorption measurements at high pressure.

Appendix

Van der Waals (VdW) Equation of State

The van der Waals equation defines the relationship between molar volume and other state properties as,

$$P(V_m, T) = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

where a ($\text{l}^2\text{bars/mol}$) and b (l/mol) are empirical van der Waals coefficients. The compressibility is found from the cubic root of this equation for V_m at a given pressure and temperature. The parameters a and b are defined for critical temperature, T_c , and critical pressure, P_c , as,

$$a = 0.421875 \frac{R^2 T_c^2}{P_c}$$

$$b = 0.125 \frac{RT_c}{P_c}$$

Redlich-Kwong (RK) Equation of State

The Redlich-Kwong (RK) [1] equation of state defines the relationship between molar volume and other state properties as,

$$P(V_m, T) = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T} V_m (V_m + b)}$$

The compressibility is found from the cubic root of this equation for V_m at a given pressure and temperature and the parameters a and b from,

$$a = 0.42748 \frac{R^2 T_c^{5/2}}{P_c}$$

$$b = 0.08664 \frac{RT_c}{P_c}$$

Redlich-Kwong-Soave (RKS) Equation of State

The Redlich-Kwong-Soave (RKS) [2] equation of state defines the relationship between molar volume and other state properties as,

$$P(V_m, T) = \frac{RT}{V_m - b} - \frac{af(T_r)}{V_m(V_m + b)}$$

The compressibility is found from the cubic root of this equation for V_m at a given pressure and temperature and the



acentric factor [3], w which accounts for difference in molecular shape and is incorporated in the factor $f(T_r)$,

$$T_r = \frac{T}{T_c}$$

$$f(T_r) = [1 + k(1 - \sqrt{T_r})]^2$$

$$k = 0.48508 + 1.55171w - 0.15613w^2$$

The parameters a , b are found using,

$$a = 0.42748 \frac{R^2 T_c^2}{P_c}$$

$$b = 0.08664 \frac{RT_c}{P_c}$$

Peng-Robinson (PR) Equation of State

The Peng-Robinson (PR) [4] equation of state defines the relationship between molar volume and other state properties as,

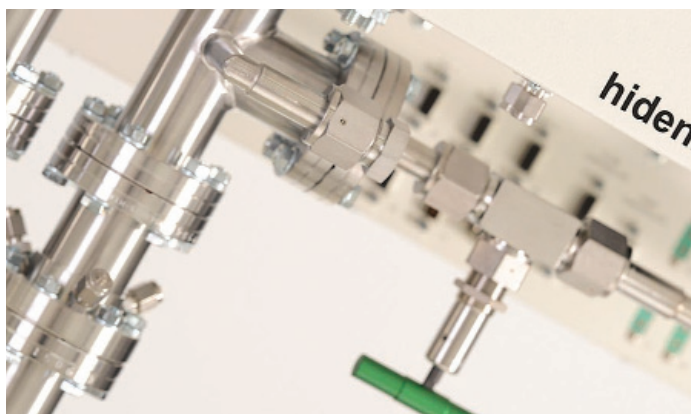
$$P(V_m, T) = \frac{RT}{V_m - b} - \frac{af(T_r)}{V_m^2 + 2bV_m - b^2}$$

The compressibility is found from the cubic root of this equation for V_m at a given pressure and temperature and the acentric factor³, w which accounts for difference in molecular shape and is incorporated in the factor $f(T_r)$,

$$T_r = \frac{T}{T_c}$$

$$f(T_r) = [1 + k(1 - \sqrt{T_r})]^2$$

$$k = 0.37464 + 0.154226w - 0.26992w^2$$



The parameters a , and b are found from,

$$a = 0.45724 \frac{R^2 T_c^2}{P_c}$$

$$b = 0.07780 \frac{RT_c}{P_c}$$

References

- [1] M. Modell and R. Reid, Thermodynamics and its Applications, Prentice Hall, Inc., New Jersey (1983) p.152.
- [2] G. Soave, Chem. Eng, Sci. 27 (1972) 1197-1203
- [3] K. S. Pitzer et al., J. Am. Chem. Soc. 77 (1955)3433-3440
- [4] D. Y. Peng and D. B. Robinson, Ind. Eng. Chem. Fundam. 15 (1976) 59-64

