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The CO_2–H_2O system: IV. Empirical, isothermal equations for representing vapor-liquid equilibria at 110–350 °C, $P \leq 150$ MPa

James G. Blencoe*

Chemical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Building 4500-S, Oak Ridge, Tennessee 37831-6110, U.S.A.

Abstract

Empirical formulae are presented for calculating vapor-liquid equilibria (VLE) in the CO_2-H_2O system at 10 temperatures between 110 and 350 °C. At each temperature, separate functions are used to represent the bubble- and dew-point boundary curves that: originate at the saturation vapor pressure of water ($P^{H_2O}_{sat}$) at $X_{CO_2} = 0$; diverge with increasing pressure up to $\sim P(X^{max}_{CO_2})$ where $\partial P/\partial X_{CO_2} = +\infty$ along the dew-point curve; then converge with increasing pressure above $P(X^{max}_{CO_2})$. At temperatures below 265 °C and pressures $> P(X^{max}_{CO_2})$, the compositions of coexisting liquid and vapor [$X^{L(V)}_{CO_2}$ and $X^{V(L)}_{CO_2}$] do not converge completely with increasing pressure due to the absence of critical behavior. Thus, relatively simple functions suffice to accurately represent VLE at those temperatures. In contrast, at $T > 265$ °C, $X^{L(V)}_{CO_2}$ and $X^{V(L)}_{CO_2}$ converge rapidly as P approaches P_c (the critical pressure in the CO_2-H_2O system at a given temperature between 265 and 374 °C and $P \leq 215$ MPa). For those temperatures, therefore, more complex VLE formulae are required to achieve close representation of phase relations. For dew-point equations, this includes adding an exponential "correction term" to ensure that $\partial P/\partial X_{CO_2} = 0$ at the critical points indicated by corresponding bubble-point functions.

Stable liquid-vapor coexistence in mixed-volatile systems requires $f^L_i = f^V_i$ (isofugacity conditions) for all "i" (volatile components) in the two fluid phases. Thus, the equations presented in this paper specify numerous P-T-X conditions where $f^L_{H_2O} = f^V_{H_2O}$ and $f^L_{CO_2} = f^V_{CO_2}$ in the CO_2-H_2O system. These results have important applications in the ongoing effort to develop a more rigorous thermodynamic model for CO_2-H_2O fluids at geologically relevant temperatures and pressures.