

efficients of methane in a mixture with hydrogen at equilibrium with solid methane (Hiza and Herring, 1965). The good agreement at these low temperatures and high pressures suggests that the revised Redlich-Kwong equation can be successfully applied to mixtures of nonpolar and quantum gases.

Conclusion

The equation of Redlich and Kwong provides a simple method for calculation of fugacity coefficients in nonpolar vapor mixtures at high pressures. The dimensionless constants Ω_a and Ω_b which are universal in the original Redlich-Kwong equation are replaced by constants evaluated from the saturated volumetric properties of each pure component. This modification is relatively unimportant for the vapor phase, although it is very important for the liquid phase (Chueh and Prausnitz, 1967b). The large improvement for vapor mixtures is obtained through a modification in the mixing rule for the equation-of-state constant, a ; for mixtures, the accuracy of the equation is significantly increased when the original, inflexible mixing rule is replaced by a flexible rule which contains one characteristic binary constant. Through effective critical constants the equation of state can also be used for mixtures containing one or more of the quantum gases. Vapor-phase fugacity coefficients calculated by this modification of the Redlich-Kwong equation are useful for reduction and correlation of high-pressure phase equilibrium data (Chueh, 1967).

Acknowledgment

The authors are grateful to the National Science Foundation for financial support and to the Computer Center, University of California, Berkeley, for the use of its facilities.

Nomenclature

a, b	= constants in Redlich-Kwong equation of state
c_1, c_2	= constants given by Equations 20 and 21
f	= fugacity
k_{ij}	= characteristic constant for i - j interaction
m	= molecular weight
m_{ij}	= molecular weight characteristic of i - j interaction; the reduced mass
N	= number of components in the mixture
n_i	= number of moles of component i
P	= total pressure
P_c	= critical pressure
P_c°	= classical critical pressure (high-temperature limit of effective critical pressure)
P_{cij}	= critical pressure characteristic of i - j interaction
R	= gas constant
T	= temperature
T_c	= critical temperature
T_c°	= classical critical temperature (high-temperature limit of effective critical temperature)
T_{cij}	= critical temperature characteristic of i - j interaction
v	= molar volume of vapor phase
v_c	= critical volume
v_c°	= classical critical volume ($v_c^\circ = 0.291RT_c^\circ/P_c^\circ$ for quantum gases)
v_{cij}	= critical volume characteristic of i - j interaction
y	= mole fraction

z	= compressibility factor
z_c	= critical compressibility factor
z_c°	= classical critical compressibility factor (0.291 for quantum gases)
z_{cij}	= critical compressibility factor characteristic of i - j interaction
ω	= acentric factor
φ_i	= fugacity coefficient of component i in a gas mixture
Ω_a, Ω_b	= dimensionless constants in Redlich-Kwong equation

SUPERScript

$\circ$ = classical

SUBSCRIPTS

c = critical

i, ii = pure component i

ij = i - j pair

Literature Cited

- Barner, H. E., Pigford, R. L., Schreiner, W. C., 31st Midyear Meeting, American Petroleum Institute, Division of Refining, Houston, Tex., May 1966.
- Beattie, J. A., *Chem. Rev.* **44**, 141 (1949).
- Chueh, P. L., dissertation, University of California, Berkeley, 1967.
- Chueh, P. L., Muirbrook, N. K., Prausnitz, J. M., *A.I.Ch.E. J.* **11**, 1097 (1965).
- Chueh, P. L., Prausnitz, J. M., "Third Virial Coefficients of Nonpolar Gases and Their Mixtures," *A.I.Ch.E. J.*, in press (1967a).
- Chueh, P. L., Prausnitz, J. M., "Vapor-Liquid Equilibria at High Pressures. Calculation of Partial Molar Volumes in Nonpolar Liquid Mixtures," *A.I.Ch.E. J.*, in press (1967b).
- Estes, J. M., Tully, P. C., *A.I.Ch.E. J.* **13**, 192 (1967).
- Evans, R. B., Watson, G. M., *Ind. Eng. Chem., Chem. Eng. Data Ser.* **1**, 67 (1956).
- Gunn, R. D., Chueh, P. L., Prausnitz, J. M., *A.I.Ch.E. J.* **12**, 937 (1966).
- Hiza, M. J., Herring, R. N., "International Advances in Cryogen Engineering," K. D. Timmerhaus, ed., Vol. 10, Section M-U, p. 182, Plenum Press, New York, 1965.
- Joffe, J., *Ind. Eng. Chem.* **40**, 1738 (1948).
- Joffe, J., Zudkevitch, D., *IND. ENG. CHEM. FUNDAMENTALS* **5**, 455 (1966).
- Johnston, H. L., White, D., *Trans. Am. Soc. Mech. Engrs.* **70**, 651 (1948).
- Leland, T. W., Chapplear, P. S., Gamson, B. W., *A.I.Ch.E. J.* **8**, 482 (1962).
- Lewis, G. N., Randall, M., "Thermodynamics," McGraw-Hill, New York, 1923.
- Mann, D. B., Natl. Bur. Std., Tech. Note 154A (1962).
- Olds, R. H., Reamer, H. H., Sage, B. H., Lacey, W. H., *Ind. Eng. Chem.* **41**, 475 (1949).
- Orentlicher, M., Prausnitz, J. M., *Can. J. Chem.*, in press (1967).
- Prausnitz, J. M., *A.I.Ch.E. J.* **5**, 3 (1959).
- Prausnitz, J. M., Gunn, R. D., *A.I.Ch.E. J.* **4**, 430 (1958).
- Reamer, H. H., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.* **42**, 534 (1950).
- Reamer, H. H., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.* **45**, 1805 (1953).
- Redlich, O., Ackerman, F. J., Gunn, R. D., Jacobson, M., Lau, S., *IND. ENG. CHEM. FUNDAMENTALS* **4**, 369 (1965).
- Redlich, O., Kwong, J. N. S., *Chem. Rev.* **44**, 233 (1949).
- Robinson, R. L., Jacoby, R. H., *Hydrocarbon Process Petrol. Refiner* **44**, No. 4, 141 (1965).
- Sage, B. H., Lacey, W. N., "Thermodynamic Properties of Lighter Hydrocarbons and Nitrogen," American Petroleum Institute, New York, 1950.
- Sage, B. H., Reamer, H. H., Olds, R. H., Lacey, W. N., *Ind. Eng. Chem.* **34**, 1108 (1942).
- Shah, K. K., Thodos, George, *Ind. Eng. Chem.* **57**, 30 (1965).
- Wilson, G. M., *Advan. Cryogenic Eng.* **9**, 168 (1964).

RECEIVED for review March 20, 1967
ACCEPTED June 5, 1967