

A Compensated-Redlich-Kwong (CORK) equation for volumes and fugacities of CO₂ and H₂O in the range 1 bar to 50 kbar and 100–1600°C

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Abstract. We present a simple virial-type extension to the modified Redlich-Kwong (MRK) equation for calculation of the volumes and fugacities of H₂O and CO₂ over the pressure range 0.001–50 kbar and 100 to 1400°C (H₂O) and 100 to 1600°C (CO₂). This extension has been designed to: (a) compensate for the tendency of the MRK equation to overestimate volumes at high pressures, and (b) accommodate the volume behaviour of coexisting gas and liquid phases along the saturation curve. The equation developed for CO₂ may be used to derive volumes and fugacities of CO, H₂, CH₄, N₂, O₂ and other gases which conform to the corresponding states principle. For H₂O the measured volumes of Burnham et al. are significantly higher in the range 4–10 kbar than those presented by other workers. For CO₂ the volume behaviour at high pressures derived from published MRK equations are very different (larger volumes, steeper $(\partial P/\partial T)_v$, and hence larger fugacities) from the virial-type equations of Saxena and Fei. Our CORK equation for CO₂ yields fugacities which are in closer agreement with the available high pressure experimental decarbonation reactions.

Introduction

Many representations of the pressure-volume-temperature (*PVT*) data for fluids in terms of equations of state may be found in the literature. One of the most important applications of these data, in the form of fugacities, $RT \ln f = \int V dP$, is in calculations on mineral equilibria at high pressures and temperatures. A major problem has been to find a single but simple equation whose functional form allows an adequate description of these thermodynamic properties over a sufficiently large range of pressure and temperature.

Various attempts to treat the non-ideal interactions between molecules have led to a variety of proposed equations of state, including the Redlich-Kwong (1949) equation which has enjoyed much well-deserved popularity in its several modified forms (MRK's e.g. Holloway

1977; Kerrick and Jacobs 1981; Bottinga and Richet 1981; Halbach and Chatterjee 1982). Although good at low to moderate pressures, the simpler MRK equations have failed to predict accurate fluid fugacities at pressures much greater than 10 kbar, and predict volumes which become progressively too large as pressure rises above a few kilobars. For example the MRK expression of Holloway (1977) yields fugacities for CO₂ which are much too high at higher pressures (Haselton et al. 1978). For H₂O, the version proposed by Halbach and Chatterjee (1982) is a significant advance in that it appears to work very well to higher pressure, but at the expense of added complexity (see the review of Ferry and Baumgartner 1987).

In an alternative approach, Saxena and Fei (1987a, b) started with the well-known virial equation of state in its isothermal, volume-explicit form:

$$z = \frac{PV}{RT} = 1 + BP + CP^2 + DP^3 \dots \quad (1)$$

As their attempts to fit high pressure fluid *PVT* experimental data with this were not entirely satisfactory, they proposed an empirical virial-like equation which seemed to work rather better, and in which a parameter *A* takes the place of the unit first term:

$$z = \frac{PV}{RT} = A + BP + CP^2 + DP^3 \dots \quad (2)$$

In this expression, the parameters, *A*, *B*, *C* and *D* are all functions of temperature. Saxena and Fei were able to represent fluid data for a large variety of molecular species with reasonable success in three pressure ranges: < 1 kbar, 1–10 kbar, and from 5 kbar up to shock-wave generated pressures. Unfortunately, for any particular fluid species, an equation of this form could not be made to represent the data at all pressures, resulting in the use of three separate pressure regions, each with its own set of parameters.

In addition to needing three pressure regions, there are two additional problems, for the petrologist, with the Saxena and Fei equations. The first stems from the fact that if the parameter *A* in Eq. (2) is not unity then the

known asymptotic approach to ideal fluid behaviour at very low pressures is violated, and this may be the cause of poor fitting of the data at pressures below about 0.5 kbar. Recognising this, Saxena and Fei reverted to Eq. (1) for pressures below 1 kbar. The second problem stems from the lack of measured PVT data in the intermediate range lying between shock-wave pressures and temperatures and the static PVT data measured below 8 kbar, and we suggest below that Eq. (2) may not interpolate accurately enough between these two ranges (see the later discussion of CO₂).

Delany and Helgeson (1978) formulated a simple PT polynomial for free energy of H₂O from 10–100 kbar based on early shock-wave data. As noted by Halbach and Chatterjee (1982) there is a discontinuity in their calculated volume, of the order of 10%, relative to Burnham et al.'s (1969) data at 10 kbar, although Delaney and Helgeson's methods avoid any such discontinuities in free energy or fugacity at this pressure.

An even more empirical formulation was used by Powell and Holland (1985) and Holland and Powell (1990) to represent the fugacity of H₂O and CO₂ at high pressures and temperatures. The original motivation came from a pragmatic desire to reduce the term $RT \ln f$ to a quadratic in temperature so that paper-and-pencil calculations for devolatilisation reactions could be made quickly and simply. In these papers, the volume integral, $RT \ln f$, was represented by a simple empirical equation in powers of pressure and temperature. While the fugacity data were adequately fitted in the range 0.3 to 30 kbar, the forms used did not allow extrapolation to pressures lower than 0.3 kbar with sufficient accuracy.

In this paper we extend the MRK equation of state with additional virial-type terms to enlarge its field of applicability to cover the range 0–50 kbar and 100–1600°C. Another motivation stems from noting the discrepancies in the calculated fugacities and volumes for CO₂ at high pressures using different equations of state, and their disagreement with the available experimentally determined decarbonation reactions.

A compensated-Redlich-Kwong (CORK) equation

We have noted that the simple MRK equations, while working extraordinarily well for low pressures, do not perform adequately at pressures much above 5 kb. Halbach and Chatterjee (1982) recognised that this failing could be compensated by allowing the parameter b in the MRK equation:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)\sqrt{T}} \quad (3)$$

to vary with pressure. By this, and an ingenious choice of the functional forms of a and b , Halbach and Chatterjee were able not only to extend the MRK equation to very high pressure but also to fit the volumes of liquid and gas in the subcritical region. This was a remarkable and satisfying achievement. The only drawback in applying their equation to the calculation of phase diagrams, is that with b a function of pressure, the volumes cannot be integrated analytically to calculate fugacities.

We propose an alternative strategy which preserves the simplicity of the MRK equation as used by Holloway (1977) and will also allow calculation of volumes and fugacities at both very high pressures and in the subcritical region. Addressing the first of these two problems, we have found that we can compensate very simply for the increasing deviation of the MRK volumes with pressure by adding on a pair of virial-type coefficients:

$$V = V_{\text{MRK}} + c\sqrt{(P - P^\circ)} + d(P - P^\circ)$$

$$\text{with } c = c_0 + c_1 T, \quad d = d_0 + d_1 T \quad (4)$$

and V_{MRK} is the volume calculated from the MRK expression (3) above.

In expression (4) P° is the pressure at which the MRK equation begins to overestimate the molar volume significantly, and may be determined from the experimental data. The second problem is to extend the simple MRK equation to subcritical conditions so that it can be used to predict the volumes of both liquid and gas along the saturation curve down to 100°C. With constant b parameter and a single temperature-dependent a parameter the MRK equation cannot perform at all satisfactorily in the subcritical region. However, if we define a separate parameter, a_{gas} , to describe the properties of the gaseous phase below T_c and allow the a parameter to describe the properties of the dense (liquid) phase below T_c as well as at supercritical conditions, we may fit the known volumetric properties quite well. The additional constraint which must be applied is that $a_{\text{gas}} = a$ at $T = T_c$. In practice we make a and a_{gas} converge at 673 K, just below T_c (695 K) and allow the critical point to be handled by the single a parameter. These relations are shown for H₂O in Fig. 1. In using Eqs. (3) and (4) the coefficient a should be used to calculate volumes at all pressures and temperatures except at pressures below the saturation curve and below 673 K, where the parameter a_{gas} should be used (see appendix).

Fitting the experimental data

H₂O data

Although there exists an extremely useful and very precise set of thermodynamic tables for water from 1 bar to

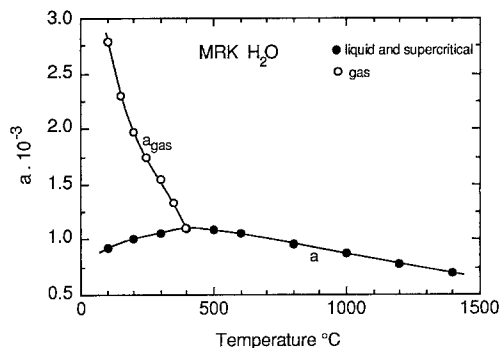


Fig. 1. Variation of the Modified Redlich Kwong a parameter for H₂O with temperature for the subcritical gaseous state (open circles) and for subcritical liquid and supercritical fluid states (solid circles). Data from Haar et al (1984)

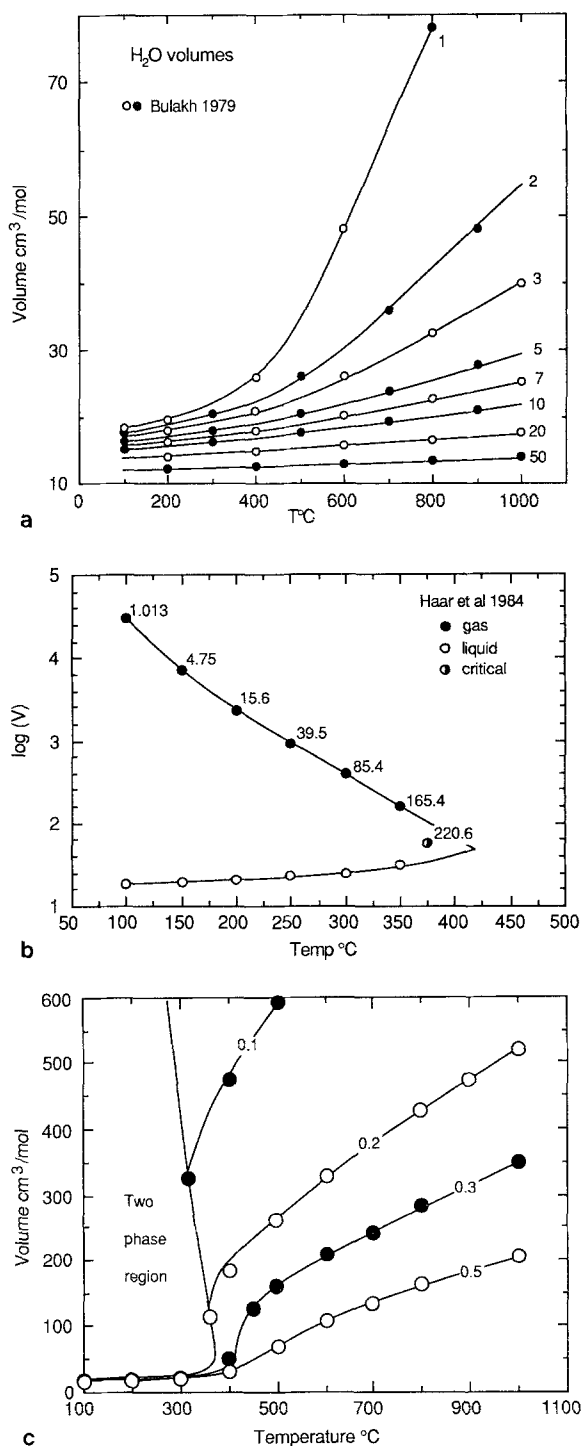


Fig. 2. a Volume of H₂O plotted against temperature, contoured for pressure using the data in Table 1; data points are from Haar et al. (1984) and Bulakh (1979). b logarithm of calculated (lines) and experimental (symbols) volume against T along the saturation curve, with pressure (in bars) indicated for each temperature. c volume data at 0.1, 0.2, 0.3 and 0.5 kbar (symbols) and 2-phase region from Haar et al. (1984) and calculated curves from data in Table 1

10 kbar together with the FORTRAN code for generating them (Haar et al. 1984), there still remains a need for an equation which covers a larger range in pressure. Although claimed to extrapolate well to 30 kbar, the extrapolated data do not agree well with the high pressure

tabulations of Bulakh (1979) and begin to deviate significantly at pressures above 10 kbar. The Haar et al. equation is a compromise between theory and empiricism, involving a 'base' equation of state, involving 8 adjustable terms which approximately fits the data coupled with an additional 10-term ideal gas formulation and a 'residual' function involving 40 empirical adjustable parameters to improve the fit.

In this work we derive coefficients for Eqs. (3) and (4) by regression of the experimental data for volumes (supplemented with some fugacity data) of H₂O. We note that there appears to be a systematic inconsistency between the volume data of Burnham et al. (1969) and those in the compilations of Bulakh (1979) and Haar et al. (1984), the Burnham et al. (1969) values being around 0.5% to 1.4% higher depending upon pressure (Fig. 2). The modified Redlich-Kwong equation of state of Halbach and Chatterjee (1982) also yields results more compatible with the lower volumes. We have therefore excluded the Burnham et al. (1969) data from the regression.

We have used the volume data from Haar et al. (1984) in the range 100–1400°C below 10 kbar together with volumes from Bulakh (1979) at higher pressures (up to 50 kbar) in regressing, using weighted least squares, for the coefficients in the pair of Eqs. (3) and (4). Because of the restrictions imposed by using the MRK equation with a constant value for b , the data are not so well fitted in the immediate vicinity of the critical point (647.3 K, 0.2206 kbar). If we optimize the volumes alone, then the calculated fugacities become a little high in the region around 400°C at high pressures because of the inability of the MRK to deal accurately with the critical region. We have elected to compromise by sacrificing the best possible fits to the volume in favour of more accurate fugacity estimation because our primary aim is to derive an equation which will yield reliable free energies for phase diagram calculations. Thus, starting with a constant value for $b = 1.46 \text{ kJ kbar}^{-1}$ (Holloway 1977) we have proceeded as follows:

a) we have determined values for a in Eq. (3) from the

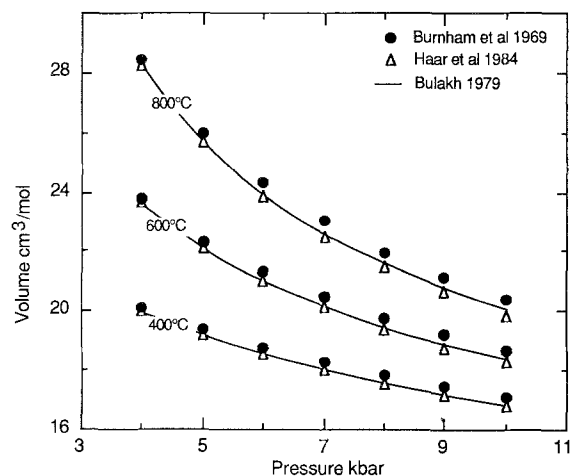


Fig. 3. Volume of H₂O plotted against pressure at 400, 600 and 800°C to show the discrepancy between the data of Burnham et al. (1969) and those of Haar et al. (1984) and Bulakh (1979). The fit from this study is very similar to the lines representing Bulakh's data

volumes of H₂O at 0.5 and 1.0 kbar in the range 100–1400°C, and for liquid H₂O along the saturation curve given by:

$$P_{\text{sat}} = -13.627 \times 10^{-3} + 7.29395 \times 10^{-7} T^2 - 2.34622 \times 10^{-9} T^3 + 4.83607 \times 10^{-15} T^5 \quad (\text{for } T < 695 \text{ K}) \quad (5)$$

with P in kbar and T in K. We have used the data of Bulakh (1979) and Haar et al. (1984) with the equations (see Fig. 1)

$$a = a_0 + a_1(673 - T) + a_2(673 - T)^2 + a_3(673 - T)^3 \quad \text{for } T < 673 \text{ K}$$

$$a = a_0 + a_4(T - 673) + a_5(T - 673)^2 + a_6(T - 673)^3 \quad \text{for } T > 673 \text{ K} \quad (6)$$

where a_0 is the value of parameter a at 673 K.

b) we have determined values for a_{gas} , using the data sources listed, from the volumes of gaseous H₂O along the saturation curve (see Fig. 1), using the same value for b as above. These data were fitted with an equation of the form:

$$a_{\text{gas}} = a_0 + a_7(673 - T) + a_8(673 - T)^2 + a_9(673 - T)^3 \quad \text{for } T < 673 \text{ K} \quad (6a)$$

c) The coefficients for Eqs. (6) and (6a) were then refined by using fugacity data from Haar et al. (1984) at 1 kbar in addition to the measured volumes, and constrained to yield the same value for a and a_{gas} at 673 K. The critical temperature, where liquid and gas phases become indistinguishable, is predicted from our CORK equation to lie at 695 K.

d) The values of the virial-type terms in Eq. (4) and final adjustments to the coefficient b were determined from regression of the measured volumes in the range 0–50 kbar and 100–1400°C. The best fits were obtained with $b = 1.465 \text{ kJ kbar}^{-1}$ and $P^\circ = 2.0 \text{ kbar}$. The values of the coefficients are given in Table 1. With this set of coefficients, we were able to fit the measured volume data to $\pm 0.49\%$ (average absolute deviation).

The quality of the fits to the data at high pressure may be seen in Fig. 2a which shows calculated and measured

volumes in the range 1 to 50 kbar. Figure 2b shows the low pressure data along the saturation curve, where the fit is extremely good except in the vicinity of the critical point. Although the volumes at and just above the critical point are not so well fitted, the measured volumes are changing extremely rapidly with pressure and temperature in this region and the equation's compromise for simplicity is acceptable for our purposes (the calculated fugacities at 1 kbar agree well with those from Haar et al. 1984: average absolute deviation in $RT \ln f \pm 0.09 \text{ kJ}$). Figure 2c shows more detail of the volume behaviour in this critical region.

Because we use two separate a parameters below 673 K, we can no longer predict the location of the saturation curve and must rely on the empirical fit of Eq. (5). The MRK equation is a cubic in volume and, below the critical temperature, has 3 real roots, the largest of which is the gas volume and the smallest the liquid volume. In using our equation, care must be used in adapting published MRK algorithms to accommodate this subcritical behaviour at $T < T_c$: in particular when $P > P_{\text{sat}}$ then the smallest real root representing the dense fluid phase (using the a parameter) must be sought; conversely, when $P < P_{\text{sat}}$ the largest real root representing the low density gaseous phase (using the a or a_{gas} parameter, depending on temperature) must be sought. At temperatures above 695 K the MRK equation yields only one real root and so no such ambiguity occurs.

In summary, the extensions to the MRK equation allow simple prediction of volumes and fugacities at all pressures to 50 kbar with 10 adjustable parameters. It should allow the calculation of phase diagrams, in conjunction with thermodynamic datasets, in a smooth and reliable manner over a very wide range of geologically relevant conditions. In deriving fugacities with these equations at temperatures below 695 K, care must be taken to integrate gas volumes up to the critical pressure and then a second integration of liquid volumes from the critical pressure to the pressure of interest must be made (see appendix).

CO₂ data

As the critical temperature and pressure of CO₂ are so low there is no complicating discontinuity in volume in the range of conditions of interest to metamorphic petrology (0–50 kbar and 100–1600°C). Volume data from Shmonov and Shmulovich (1974) were used in the 1–8 kbar range together with the precise volumes measured at 1 atmosphere by McCormack and Schneider (1950) and up to 500 bar by Vukalovich and coworkers (data in Vukalovich and Altunin 1968). The absence of any measured CO₂ volume data in the high pressure range (10–50 kbar) means that we must rely, at present, on equation of state extrapolations from lower pressures together with interpolations between these low pressures and the shock-wave PT range (Bottinga and Richet 1981; Saxena and Fei 1987a) for data above 10 kbar. These two datasets predict volumes quite differently above 10 kbar, Fig. 4. In particular the Saxena and Fei (SF) equation yields lower values of both volume and isochore slope at high temperatures and

Table 1. Parameters for Eqs. 3, 4 and 6a, b (see text)

	H ₂ O	CO ₂
b	1.465	3.057
a :		
a_0	1113.4	741.2
a_1	−0.88517	−0.10891
a_2	4.5300×10^{-3}	$−3.4203 \times 10^{-4}$
a_3	$−1.3183 \times 10^{-5}$	
a_4	−0.22291	
a_5	$−3.8022 \times 10^{-4}$	
a_6	1.7791×10^{-7}	
a_{gas} :		
a_7	5.8487	
a_8	$−2.1370 \times 10^{-2}$	
a_9	6.8133×10^{-5}	
c :		
c_0	$−3.025650 \times 10^{-2}$	$−2.26924 \times 10^{-1}$
c_1	$−5.343144 \times 10^{-6}$	7.73793×10^{-5}
d :		
d_0	$−3.2297554 \times 10^{-3}$	1.33790×10^{-2}
d_1	2.2215221×10^{-6}	$−1.01740 \times 10^{-5}$
P°	2.00	5.00

Units: T (K), P (kbar), V (kJ/kbar), a ($\text{kJ}^2 \text{kbar}^{-1} \text{K}^{1/2} \text{mol}^{-2}$), b ($\text{kJ kbar}^{-1} \text{mol}^{-1}$)

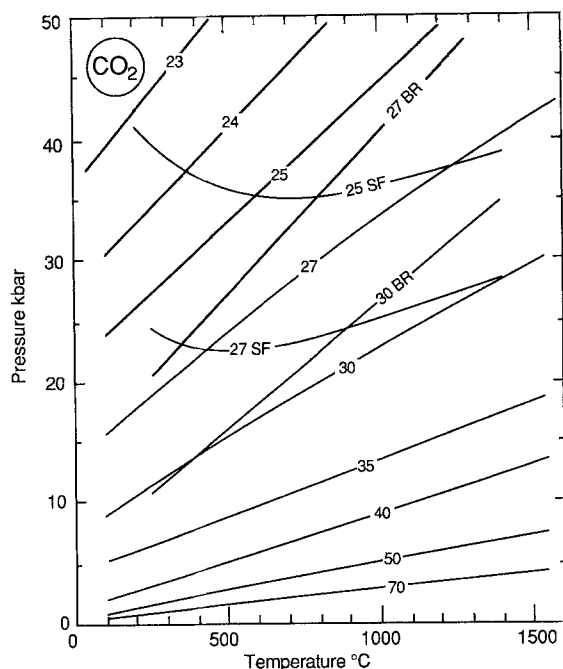


Fig. 4. Comparison of calculated PVT data for CO_2 . BR: Bottinga and Richet (1981). SF: Saxena and Fei (1987a). Unlabelled: equations from this work. Isochores in $\text{cm}^3 \text{mol}^{-1}$.

pressures than that of Bottinga and Richet (BR). The behaviour of the SF equation leads to a somewhat unsatisfactory curvature and reversal of isochore slope below 600–700°C (Fig. 4). As will be shown below, the BR equation yields larger fugacities and higher temperatures for calculated decarbonation reactions than the SF equation.

Comparing high pressure fugacity data for CO_2

The MRK extrapolation of CO_2 fugacity has been evaluated by Haselton et al. (1978) who have already noted that the computed fugacities are somewhat high in comparison to those required by experimentally-determined decarbonation reactions. The situation has improved since then in that we are able now to use internally-consistent thermodynamic datasets (e.g. Berman 1988; Holland and Powell 1990) to minimize errors in the thermodynamic properties of the solid phases in the reactions used to evaluate the CO_2 data. Here we will make use of the dataset of Holland and Powell (1990) to calculate the PT locations of the following decarbonation reactions:

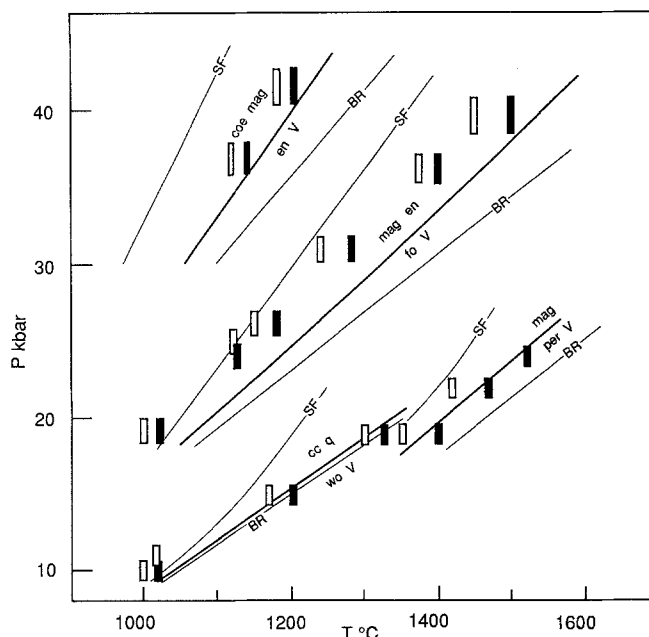
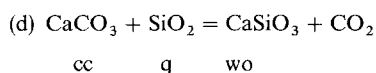
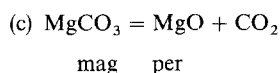
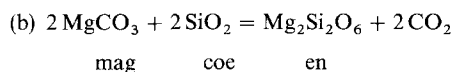
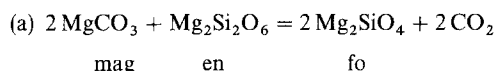


Fig. 5. A PT diagram showing the experimental equilibria for decarbonation reactions at high pressure, and the calculated positions of these reactions using the SF (Saxena and Fei 1987a) and BR (Bottinga and Richet 1981) CO_2 datasets. Bold lines are calculated from the data in Table 1. Experiments of Haselton et al. (1978), Eggler et al. (1979), Newton and Sharp (1975) and Irving and Wyllie (1975). Symbols show approximate uncertainty due to friction correction errors.

We show the calculated results for these four reactions in Fig. 5, using the high pressure fugacity datasets based on Bottinga and Richet (1981) and Saxena and Fei (1987a) together with the experimental brackets. It is clear that the BR data systematically overestimate the decarbonation temperatures while the SF data systematically underestimate them. With the exception of reaction (a) the two sets of data disagree about equally with the experiments, and it would be tempting to suggest, setting aside the problem of the isochore behaviour in the SF equation, that a simple average of the two would produce acceptable results at high temperatures. However, we are unwilling to use the phase equilibrium experiments to retrieve fugacities as both they and the thermodynamically calculated equilibria are subject to large possible errors. As one example, the usual friction correction applied to piston-cylinder experiments at high pressures is of the order of 0–12% of the nominal run pressure; if this is so, then the nominal brackets for reaction (b) at 45 kbar could possibly be reduced by up to 5.5 kbar. Inspection of Fig. 1 of Haselton et al. (1978) indicates that they applied a 7% correction to their measured bracket. The magnitude of the friction correction depends not only on the run geometry (diameter and internal design of the pressure chamber components) and the pressure medium (talc, salt, glass, etc.) but also on temperature, and this can lead to systematic uncertainties on PT slopes of reactions at such high pressures.

In addition the PT locations of the magnesite decarbonation reactions may be rather sensitive to the volume

behaviour of magnesite at high pressures and temperatures (Urs Mader, personal communication). We have investigated the effects of varying the compressibility and thermal expansion of magnesite on reaction (a) and find that a 30% change in compressibility for magnesite makes only a trivial difference ($< 7^\circ\text{C}$ at 40 kbar). Similarly, using a quadratic pressure dependence for the volume, as in Berman (1988), in place of the simpler linear dependence used here makes no perceptible difference to the calculations. The combined uncertainties in volume and pressure measurement to 60 kbar are such that a non-linear behaviour is not warranted by the data. However, the thermal expansion of magnesite, measured up to 500°C by Markgraf and Reeder (1985), appears anomalously high and increases dramatically with temperature (Fig. 6). If the thermal expansion were extrapolated to 1500°C with the equation and coefficients of Berman (1988) it would lead to more than 12% increase in the volume of magnesite and would lower the decarbonation temperature for reaction (a) by about 60°C at 40 kbar. However, the thermal expansion is most unlikely to continue changing so rapidly—note that calcite only shows this anomalous behaviour up to its disordering temperature (960°C ; Redfern et al. 1989) which occurs when the volume has increased by only 3%. We suspect that a similar CO_3 rotational disordering process in magnesite may be the cause of the anomalous thermal expansion, but cannot guess the temperature at which such disorder may go to completion; thus, we prefer not to extrapolate the volume as a quadratic in temperature but to take the simpler linear equations used in Holland and Powell (1990) which appear reasonable enough for describing the behaviour of the other phases (see Fig. 6). An additional complication is that the compressibility will increase along with the thermal expansion as temperature rises; we have no information to test the magnitude of this effect, but note that it would have a compensating effect on the location of reaction (a), again tending to favour simple linear extrapolations of volume behaviour until our knowledge of the PT dependence of mineral volumes

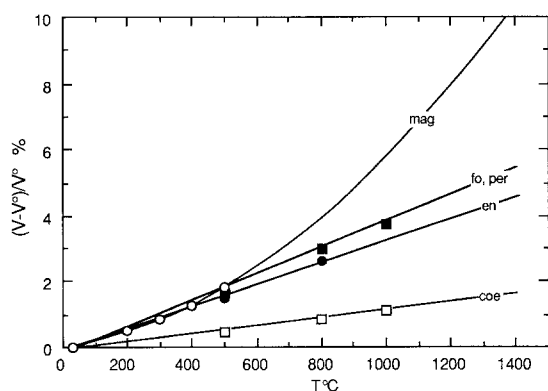


Fig. 6. Volume thermal expansion of magnesite, coesite, enstatite, forsterite and periclase. Magnesite data are only measured up to 500°C and show anomalous behaviour, possibly due to CO_3 orientational disordering, and the quadratic extrapolation used by Berman (1988) is shown here. The linear extrapolation used in Holland and Powell (1990) would be approximately coincident with the curve for forsterite. Extrapolation is highly uncertain (see text)

improves. If it turns out that the thermal expansion of magnesite continues to increase dramatically with temperature, then the equations of BR will be in somewhat closer agreement with the experiments. What is required is an equation which behaves rather similarly to BR's MRK, but which yields lower volumes and fugacities at high pressure.

A new CORK equation for CO_2

We derive a new representation for CO_2 using the same approach as for H_2O , using virial-type terms to compensate for the tendency of the MRK equation to yield volumes which are too high at high pressures. We have accepted as a database the experimental volumes of Shmonov and Shmulovich (1974), Kennedy and Holser (1966), and Tsiklis et al. (1971) in the range 0.3 to 8 kbar, the volume data from Vukalovich and Altunin (1968) and McCormack and Schneider (1950) at and below 0.5 kbar, together with equation of state interpolations and extrapolations for volume (Shmulovich and Shmonov 1975; Bottinga and Richet 1981) in the range $200\text{--}1600^\circ\text{C}$ and 0.1–8 kbar. To help constrain the volumes at high pressures, we have taken several observations into account:

- (1) We have graphically extrapolated the isochores from the experimental data, using the systematic pressure dependence shown by the isochore slopes $(\partial P/\partial T)_v$. Slopes are intermediate between those generated by SF and BR, but closer to BR.
- (2) We note that at constant pressure and high temperatures the slope $(\partial V/\partial T)_p$ is approximately constant and that it depends linearly on $1/P$ in the range 1–8 kbar. We have extrapolated these slopes to high pressures on this basis.
- (3) Volumes were extrapolated to high pressures by plotting them against $1/\sqrt{P}$, which shows a smooth behaviour.
- (4) The three factors above allow graphical determination of a preliminary set of isochores in the range $100\text{--}1600^\circ\text{C}$, 10–60 kbar. Finally, the isochores were adjusted slightly to yield volumes between those of BR and SF, but closer to BR, at high temperatures and pressures, in keeping with our conclusions based on the experimental decarbonation reactions.

The graphically derived volumes to 60 kbar were added to the experimental dataset discussed above and a modification of Eqs. (3) and (4) were fitted to them by least squares. For CO_2 the a parameter can be represented by a simple quadratic in temperature

$$a = a_0 + a_1 T + a_2 T^2 \quad (373 < T < 1873 \text{ K})$$

whose coefficients are given in Table 1.

Because there are no complications of critical phenomena in the PT range considered, we can simplify the CORK equation further to yield a convenient volume-explicit equation. Equation (3) may be rearranged as:

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

and substituting the approximation $V \approx RT/P + b$ on the

right hand side leads to:

$$V \approx \frac{RT}{P} + b - \frac{aR\sqrt{T}}{(RT + bP)(RT + 2bP)}. \quad (7)$$

As for H₂O, we add on two virial-like terms to improve the high pressure behaviour

$$V \approx \frac{RT}{P} + b - \frac{aR\sqrt{T}}{(RT + bP)(RT + 2bP)} + c\sqrt{P} + dP \quad (7a)$$

Equation (7a) may be simply integrated to yield fugacities:

$$RT \ln f = RT \ln(1000 P) + bP + \frac{a}{b\sqrt{T}} \{ \ln(RT + bP) - \ln(RT + 2bP) \} + \frac{2}{3} c P\sqrt{P} + \frac{d}{2} P^2 \quad (8)$$

This simplified Eq. (7a), has been fitted to the experimental data in order to derive values for the parameters. In particular, Eq. (7a) leads to a best value for $b = 3.7852$ kJ/kbar which is somewhat larger than Holloway's (1977) value of $b_{\text{MRK}} = 2.97$ kJ/kbar. This is to be expected, given the nature of the simplifications made in deriving (7a), and we note that the parameter b , using the full Eqs. (3, 4), is very close to Holloway's value (Table 1). Parameters a , c , and d are all linear in temperature and are given in Table 2 (in corresponding states form, see below). Surprisingly, the quality of fit of the shorter CORK Eqs. (7, 8) is marginally better than the longer CORK Eqs. (3, 4) using the average absolute deviation ($\pm 0.77\%$ AAD, and $\pm 0.84\%$ AAD respectively) as a measure.

As shown later, the CORK equations probably allow safe extrapolations to very high temperatures and, we believe, lead to results which are similar to and improve on those generated from BR's equation by (a) lowering the calculated volumes at high pressures and temperatures and (b) shallowing the slopes of the isochores. The predictions of the decarbonation reactions from our equations are shown in Fig. 5. A slight increase in the thermal expansion of magnesite (over and above that of the linear estimates of Holland and Powell 1990) but lower than the quadratic extrapolation (Fig. 6) would lead to a closer agreement with the experimental brackets.

The fit of the data is compared with measured volumes of Shmonov and Shmulovich (1974) and Tsiklis et al. (1971) in Fig. 7. The equation fits the volume data below 8 kbar with an average absolute deviation of $\pm 0.7\%$ and above 8 kbar of $\pm 0.8\%$.

Table 2. Corresponding states parameters for Eqs. 9 (see text)

a :	a_0	5.45963×10^{-5}
	a_1	-8.63920×10^{-6}
b :	b_0	9.18301×10^{-4}
	c_0	-3.30558×10^{-5}
c :	c_1	2.30524×10^{-6}
	d_0	6.93054×10^{-7}
d :	d_1	-8.38293×10^{-8}

Units: T (K), P (kbar), V (kJ/kbar), a (kJ² kbar⁻¹ K^{1/2} mol⁻²), b (kJ kbar⁻¹ mol⁻¹)

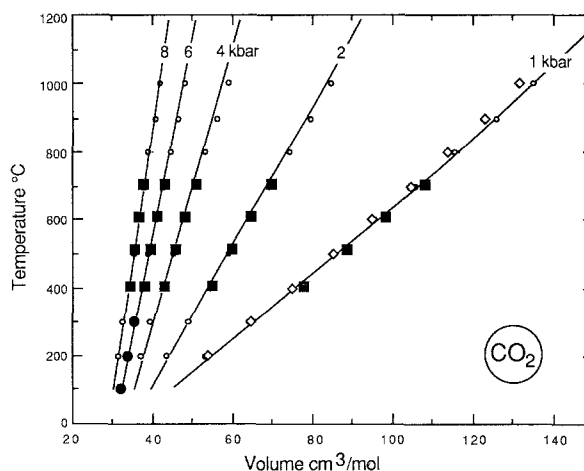


Fig. 7. Volume of CO₂ plotted against temperature, contoured for pressure using the equation in Table 1. Symbols: *small circles*, equation of state of Shmulovich and Shmonov (1975); *filled squares*, experimental data of Shmonov and Shmulovich (1974); *filled circles*, experiments of Tsiklis et al. (1971); *diamonds*, data of Kennedy and Holser (1966)

Extensions to other gases, Corresponding states

Saxena and Fei (1987b) noted that their corresponding states equations fitted the measured volume data for CO₂ extremely well. In consequence, our CORK equation, fitted to the data for CO₂, should be able to predict volumes and fugacities for several other gases which are known to obey approximately the principle of corresponding states. We may use Eqs. (7a) and (8) directly for any gas by defining the parameters in terms of the critical temperature (T_c) and critical pressure (P_c) as follows:

$$\begin{aligned} a &= a_0 \frac{T_c^{5/2}}{P_c} + a_1 \frac{T_c^{3/2}}{P_c} T \\ b &= b_0 \frac{T_c}{P_c} \\ c &= c_0 \frac{T_c}{P_c^{3/2}} + \frac{c_1}{P_c^{3/2}} T \\ d &= d_0 \frac{T_c}{P_c^2} + \frac{d_1}{P_c^2} T, \end{aligned} \quad (9)$$

where a_0 , a_1 , b_0 , c_0 , c_1 , d_0 and d_1 are the universal constants given in Table 2. For example, the parameters for CO₂ would be found by substituting $T_c = 304.2$ and $P_c = 0.0738$ kbar into the expressions (9) above.

The predictions of volume for CH₄, CO and H₂ from Eq. (7a) are shown in Fig. 8. The results for CH₄ are comparable to, and those for CO are slightly better than, the predictions from the equation of Saxena and Fei (1987b) if we accept the interpolation and extrapolations of Mel'nik (1978). For H₂ Eq. (7a) works reasonably well if the critical pressure and temperature are taken as 0.0211 kbar and 41.2 K, i.e. 0.008 kbar and 8 K larger than the measured values to take into account quantum effects (Ryzhenko and Volkov 1971). The fact that the volume for H₂ can be approximated up to at least 873 K suggests that the equation derived here for CO₂ should be

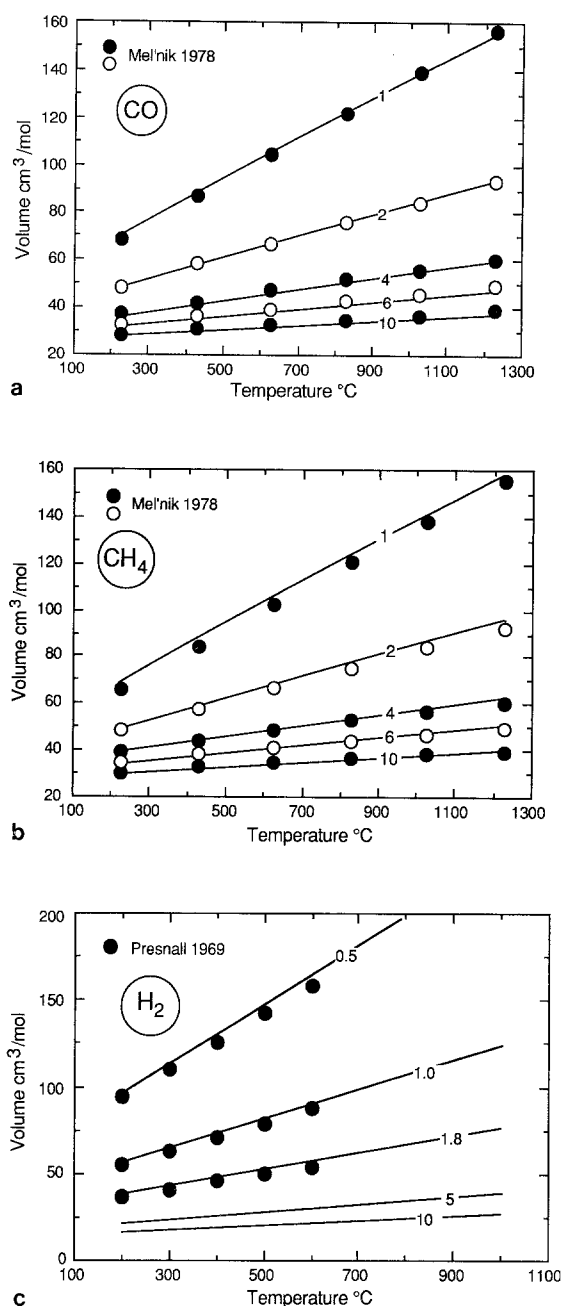


Fig. 8a-c. Volume-temperature plots for CO, CH₄, and H₂ comparing the volumes calculated from the data in Table 1 and Eq. (7a) with those from Mel'nik (1978) and Presnall (1969). *P* in kbar.

Critical constants used for gases in Fig 8

gas	<i>T_c</i> (K)	<i>P_c</i> (kbar)
CO ₂	304.2	0.0738
CH ₄	190.6	0.0460
H ₂	41.2	0.0211
CO	132.9	0.0350

reliable up to temperatures of around 6500 K. Equation (7a) should provide reasonable estimates for volume and fugacity for CO, O₂, CH₄, N₂, H₂, and perhaps for other gases such as H₂S and SO₂, over the range 100–1600°C and up to 50 kbar.

Conclusions

A compensated-Redlich-Kwong (CORK) equation of state appears capable of describing volumes and fugacities of H₂O and CO₂ to 50 kbar, and fits the volume data well ($\pm 0.5\%$ for H₂O and $\pm 0.7\%$ for CO₂) in all but the near-critical region. The equation of state for CO₂ of Bottinga and Richet (1981) appears systematically to overestimate, and that of Saxena and Fei (1987a) to underestimate, high pressure volumes and fugacities. There is clearly a great need for further measurements on either fugacity or volume of CO₂ at pressures in the 10–50 kbar range. Our equation for CO₂ appears to yield results in closer agreement with the high pressure decarbonation experiments and, in corresponding state form, may be useful in estimating fugacity or volume behaviour of many fluids over large ranges in temperature and pressure.

Appendix

Calculation of CORK volumes

Volumes may be readily calculated from the CORK equations by summing the two components of Eqs. (3) and (4). The MRK component, V_{MRK} , is found by rearranging the MRK expression as a cubic in volume:

$$PV_{\text{MRK}}^3 - RTV_{\text{MRK}}^2 - \left(bRT + b^2P - \frac{a}{\sqrt{T}}\right)V_{\text{MRK}} - \frac{ab}{\sqrt{T}} = 0 \quad \text{A.1}$$

Solution of the cubic equation above may follow standard algorithms (e.g. Press et al. 1989, section 5.5) or by Newton's method (e.g. Press et al. 1989, section 9.4). If using Newton's method, care must be taken to ensure that the initial guess for the dense phase below T_c (695 K) takes a suitably low value such as $V_{\text{init}} = b/2$ and for the gaseous phase takes a suitably high value such as $V_{\text{init}} = RT/P + 10b$ to ensure convergence to the correct root. Above T_c there is only one real root and a suitable initial guess can be taken as $V_{\text{init}} = RT/P + b$.

The virial component of volume is determined from the second and third terms in Eq. (4) and added to the MRK component, if the pressure is above P° .

Calculation of CORK fugacities

Fugacities may be calculated by summing both the MRK and virial components to the CORK model. Firstly, the volume at the desired P and T must be found by rearranging the MRK part of the CORK Eq. (3) and solving the cubic equation in volume as discussed above. The virial contribution to the volume may then be added (Eq. 4), and the compressibility factor $z = PV/RT$ determined. The fugacity coefficient $\gamma = f/P$ is then given by (e.g. Redlich and Kwong 1949)

$$\ln \gamma = z - 1 - \ln(z - B) - A \ln\left(1 + \frac{B}{z}\right) + \ln \gamma_{\text{virial}} \quad \text{A.2}$$

$$\ln \gamma_{\text{virial}} = \frac{1}{RT} \left[\frac{2}{3} c(P - P^\circ)^{1.5} + \frac{d}{2} (P - P^\circ)^2 \right] \quad \text{A.3}$$

where $B = \frac{bP}{RT}$ and $A = \frac{a}{bRT^{1.5}}$ and the $\ln \gamma_{\text{virial}}$ term is only added when $P > P^\circ$.

For CO₂ these equations may be applied directly at all conditions in the range 100–1600°C and 0–50 kbar. For H₂O, because of critical phenomena, there are 3 different regions of PT space in

which the methods of calculating the fugacity are different:

(A) At temperatures above 695 K, $\ln \gamma$ may be found from Eqs. A.2 and A.3 directly. In this region the parameter a is taken from Table 1.

(B) At temperatures below 695 K and at pressures below P_{sat} , $\ln \gamma$ may be found from Eqs. A.2 and A.3 directly. In this region the a parameter is replaced with a_{gas} (taken from Table 1) for temperatures below 673 K.

(C) At temperatures below T_c (695 K) and at pressures above P_{sat} , care must be taken to evaluate the fugacities by noting the integration limits: integration must be performed from 1 bar to P_{sat} and then from P_{sat} to the pressure of interest in the MRK part of the fugacity coefficient calculation. In practice this is most easily performed as follows:

- (1) Evaluate z_1 and $\ln \gamma_1$, the compressibility factor and logarithm of fugacity coefficient of the gaseous phase, at the saturation pressure P_{sat} (found from Eq. 5) using Eqs. A.1, A.2 and A.3 with the a_{gas} parameter (or a if $T > 673$ K) from Table 1.
- (2) Evaluate z_2 and $\ln \gamma_2$ for the dense (liquid) phase from Eqs. A.1, A.2 and A.3 at P_{sat} using the a parameter from Table 1.
- (3) Evaluate z_3 and $\ln \gamma_3$ for the fluid phase at the pressure of interest, P , from Eqs. A.1, A.2 and A.3 using the a parameter from Table 1.
- (4) The value for $\ln \gamma$ at the pressure of interest, P , is then given by summing the terms: $\ln \gamma = \ln \gamma_1 - \ln \gamma_2 + \ln \gamma_3$

Note: the CORK volume and fugacity behaviour is contiguous rather than continuous at 673 K, exhibiting a discrete, but small, change in slope at this temperature.

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