SOP 24

Calculation of the fugacity of carbon dioxide in the pure gas or in air.

1. Scope and field of application

This procedure describes a method for the calculation of the fugacity of carbon dioxide in the pure gas or in air. The fugacity, $f(CO_2)$, is expressed either in Pascals or in atmospheres (Note 1).

2. Definition

The chemical potential (μ_B) of an individual component of a vapor phase can be expressed in terms of its fugacity (f_B). This is defined by the equation

$$RT \ln f_B = \mu_B - \lim_{p \to 0} (\mu_B - RT \ln(x_B p / p^\circ)) \qquad (1)$$

where x_B is the mole fraction of B in the gaseous mixture and thus $x_B p$ is the partial pressure of B (p_B) in the vapor phase and p° is astandard pressure (typically 101325 Pa, *i.e.* 1 atm). The term

$$\lim_{p \to 0} (\mu_B - RT \ln(x_B p / p^\circ)) \qquad (2)$$

is thus a standard chemical potential, $\mu_B^\circ(T)$.

3. Principle

The vapor phase fugacity of either a pure gas ($x_B = 1$) or of a component in a mixture of gases can be calculated from the equation

$$f_B = x_B p \exp\left(\int_0^p \frac{(V_B - RT/p')dp'}{RT} \right) . \qquad (3)$$

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1   1 atm = 101325 Pa.

V_B is obtained from

$$V_B = \left(\frac{\partial V}{\partial n_B}\right)_{T,\,p} \;, \tag{4}$$

where V is given by an equation of state for the vapor:

$$V = f(T, p) \;. \tag{5}$$

3.1 The ideal gas equation

The simplest equation of state is the expression for a perfect gas mixture

$$V = \left(\sum_B n_B\right) RT / p \;. \tag{6}$$

The integral in equation (3) is then equal to zero and

$$f_B = x_B p \;. \tag{7}$$

3.2 The virial equation

More generally the equation of state can be represented by a virial expression:

$$\frac{p V_B}{RT} = 1 + \frac{B(T)}{V_B} + \frac{C(T)}{V_B^2} + \ldots \tag{8}$$

This equation, truncated after the second virial coefficient is usually adequate to represent p–V–T properties at pressures up to a few atmospheres. It also has the advantage that the coefficient $B(T)$ can be related to the intermolecular potential energy function of the molecules concerned.

In a mixture of gases,

$$B(T) = \sum_l \sum_m x_l x_m B_{lm}(T) \;, \tag{9}$$

where $B_{lm} = B_{ml}$. The total volume can then be written

$$V = \sum_k n_k V_k = \sum_k n_k \frac{RT}{p} + \frac{\sum_l \sum_m n_l n_m B_{lm}(T)}{\sum_k n_k} \;. \tag{10}$$

The partial molar volume of an individual component

$$V_B = \frac{RT}{p} - \frac{\sum_l \sum_m n_l n_m B_{lm}(T)}{\left(\sum_k n_k\right)^2} + \frac{2 \sum_m n_m B_{Bm}(T)}{\sum_k n_k} \tag{11}$$

and thus

$$V_{\mathrm{B}} = \frac{RT}{p} + \sum_l \sum_m x_l x_m (2B_{\mathrm{B}m}(T) - B_{lm}(T))p \quad . \tag{12}$$

The fugacity is then given by

$$f_{\mathrm{B}} = x_{\mathrm{B}} p \exp\left(\frac{\sum_l \sum_m x_l x_m (2B_{\mathrm{B}m}(T) - B_{lm}(T))p}{RT} \right) \quad . \tag{13}$$

For a pure gas this reduces to

$$f_{\mathrm{B}} = p \exp\left(\frac{B_{\mathrm{BB}}(T)p}{RT} \right) \quad , \tag{14}$$

where $B_{\mathrm{BB}}(T)$ is the virial coefficient for the pure gas B.

A further particular case of equation (13) is the expression for a component of a binary mixture

$$f_{\mathrm{B}} = x_{\mathrm{B}} p \exp\left(\frac{(B_{\mathrm{BB}}(T) + 2x_C^2 \delta_{\mathrm{B-C}}(T))p}{RT} \right) \quad , \tag{15}$$

where

$$\delta_{\mathrm{B-C}} = B_{\mathrm{BC}} - \tfrac{1}{2}(B_{\mathrm{BB}} + B_{\mathrm{CC}}) \quad . \tag{16}$$

Many of the cross virial coefficients for the practical computation of fugacity in vapor mixtures have never been measured experimentally. However a number of empirical approaches can be used.

The simplest of these is the Lewis and Randall rule

$$f_{\mathrm{B}} = x_{\mathrm{B}} f_{\mathrm{B}}^* \quad , \tag{17}$$

where f_{B}^* is the fugacity of pure component B at the same temperature and total pressure as the mixture—equation (14).

An alternate method of predicting $B(T)$, based on statistical-mechanical arguments, is to use the expression

$$B(T) = 2\pi L \int_0^\infty [1 - \exp\{-u(r)/kT\}] r^2 dr \quad , \tag{18}$$

where L is the Avogadro constant and k the Bolzmann constant. Here, $u(r)$—the pair-interaction energy—is assumed to depend only on the separation r of the centers of mass of two molecules.

4. Calculation and expression of results

4.1 *Virial coefficient of pure carbon dioxide*

The first virial coefficient of CO_2, $B(CO_2, T)$, is given by the expression (Weiss, 1974) which is based on values reported by Levelt-Sengers, Klein, & Gallagher (1971)

$$\frac{B(CO_2, T)}{cm^3 \cdot mol^{-1}} = -1636.75 + 12.0408 \left(\frac{T}{K}\right)$$

$$-3.27957 \times 10^{-2} \left(\frac{T}{K}\right)^2 + 3.16528 \times 10^{-5} \left(\frac{T}{K}\right)^3 , \quad (19)$$

where $265 < (T/K) < 320$.

This expression can then be used in equation (14) to calculate the fugacity of pure CO_2 provided that the pressure and temperature of the CO_2 are known.

4.2 *Virial coefficient of carbon dioxide in air*

In addition, Weiss used the Lennard-Jones (6–12) potential to estimate $u(r)$ and hence calculate values for δ_{BC} for the binary mixture: CO_2– air. He found that the temperature dependence of this parameter is represented by the equation

$$\frac{\delta(CO_2 - air)}{cm^3 \cdot mol^{-1}} = 57.7 - 0.118 \left(\frac{T}{K}\right) , \quad (20)$$

where $273 < (T/K) < 313$.

This expression can then be used in equation (15), together with equation (19), to calculate the fugacity of CO_2 in air.

4.3 *Example calculations*

4.3.1 *Fugacity of pure CO$_2$*

$T = 298.15$ K ;

$p = 101.325$ kPa (1 atm) .

Then

$$B(T) = -123.2 \ cm^3 \cdot mol^{-1} ,$$

$$f(CO_2) = 101325 \ \exp\left(\frac{-123.2 \times 10^{-6} \times 101325}{8.31451 \times 298.15}\right)$$

$$= 100.816 \ kPa ,$$

or

$$f(CO_2) = 100.816/101.325 = 0.99498 \ atm .$$

4.3.2 Fugacity of CO$_2$ in air

    T = 298.15 K ;

    p = 101.325 kPa (1 atm) ;

    $x(CO_2)$ = 350×10^{-6} .

Then

    $B(T)$ = -123.2 cm$^3 \cdot$mol^{-1} ,

    $\delta(CO_2\text{–air})$ = 22.5 cm$^3 \cdot$mol^{-1} ,

$$f(CO_2) \; = \; 350 \times 10^{-6}(101325) \; \times$$

$$\exp\left(\frac{(-123.2 \times 10^{-6} + 2(1 - 350 \times 10^{-6})^2(22.5 \times 10^{-6})) \times 101325}{8.31451 \times 298.15}\right) \quad ,$$

$$= 35.35 \text{ Pa} \quad (348.9 \times 10^{-6} \text{ atm}) .$$

References

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