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Equation of State for Solid Carbon Dioxide Based on the Gibbs Free Energy

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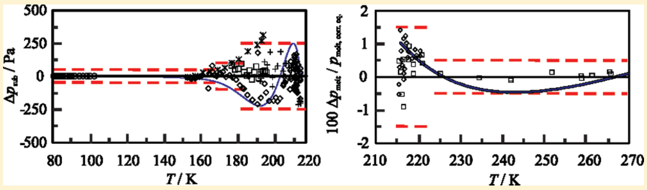
ABSTRACT: In this work a fundamental equation of state explicit in the Gibbs free energy was established, which was fitted to experimental data (heat capacity, molar volume, expansion coefficient, and compressibility) of solid carbon dioxide. Almost all of the data that the equation was fitted to are represented within the experimental uncertainty given by the authors. However, only very limited data for the thermodynamic properties of solid carbon dioxide are available. The new equation behaves physically reasonably within its range of validity. Sublimation and melting pressures of dry ice are predicted accurately using Gibbs energies calculated from the new dry ice equation and from the fundamental equation by Span and Wagner for the fluid phase (*J. Phys. Chem. Data* **1996**, *25*, 1509−1596). The results agree with those of the reference equations for sublimation and melting pressure published by Span and Wagner mostly within the uncertainty given for these equations. The resulting sublimation and melting pressures are very sensitive to variations of the Gibbs energy. The use of another equation of state for the fluid phase has a significant impact on the calculated equilibrium pressures. It is shown that the equation for dry ice also might be used for the calculation of equilibria with dry ice in the solid phase and mixtures in the fluid phase.



INTRODUCTION

Planning and dimensioning of pipelines for the transport of CO_2 in carbon capture and storage (CCS) applications require highly accurate thermodynamic property models for pure carbon dioxide as well as for CO_2-rich mixtures with impurities (e.g., N_2). Since scenarios with sharp expansion are conceivable, phase equilibria involving solid and liquid as well as solid and gas may occur. Simple correlation equations for the sublimation pressures and the melting pressures as a function of temperature can be very accurate but do not allow for flash calculations. For this reason a fundamental equation of state for dry ice based on the Gibbs free energy was established, following a general approach described by Tillner-Roth.[1] Functions for the isobaric heat capacity along an isobar and the temperature and pressure dependence of the molar volume (thermal equation of state) are required, which upon integration yield the Gibbs free energy of solid carbon dioxide.

EQUATION OF STATE

The Gibbs free energy may be written as:

$$g(p, T) = h_0 - Ts_0 + \int_{T_0}^{T} c_p(T, p_0)\,\mathrm{d}T - T\int_{T_0}^{T} \frac{c_p(T, p_0)}{T}\,\mathrm{d}T + \int_{p_0}^{p} v(p, T)\,\mathrm{d}p \tag{1}$$

In this equation, $c_p(T, p_0)$ is the isobaric heat capacity along an isobar p_0, $v(T, p)$ is a thermal equation of state explicit in the molar volume, and h_0 and s_0 are integration constants. Hence a model for the isobaric heat capacity at p_0 and a thermal equation of state for dry ice are needed to integrate eq 1. Some simplifying assumptions have to be made since only few experimental data are available for solid carbon dioxide and experimental data in the pressure range from 0 MPa to the triple point pressure p_{tr} were mostly measured along the sublimation curve:

1. The pressure dependence of $c_p(T, p)$ is negligible for 0 MPa $< p < p_{\mathrm{tr}}$.
2. The pressure dependence of the thermal expansion coefficient $\alpha(T, p)$ is negligible for 0 MPa $< p < p_{\mathrm{tr}}$.
3. The pressure dependence of the compressibility $\kappa(T, p)$ is negligible for 0 MPa $< p < p_{\mathrm{tr}}$.

The impact of these assumptions will be analyzed in the discussion. For the heat capacity a functional form proposed by Feistel and Wagner[2] was used and slightly modified:

$$c_p(T, p_0) = \frac{aT^5 + bT^3}{T^4 + cT^2 + d} \tag{2}$$

By a nonlinear least-squares fit (which was chosen for all fitting done in this work) the constants a, b, c, and d were fitted to data of Giauque and Egan.[3] As also pointed out by Manzhelii et al.,[4] the experimental data by Giauque and Egan[3] are considered the most accurate experimental data for the heat capacity of dry ice over a wide temperature range.

The required thermal equation of state is split into two parts. An equation for the expansion coefficient along an isobar and an equation for the first derivative of the molar volume with respect to pressure as a function of temperature and pressure are needed. Once these two functions are given, the molar volume may be

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obtained by integration of the total differential:

$$v - v_0 = \int_{v_0}^{v} \mathrm{d}v = \int_{T_0}^{T} \frac{\partial v}{\partial T}(T, p_0)\,\mathrm{d}T + \int_{p_0}^{p} \frac{\partial v}{\partial p}(T, p)\,\mathrm{d}p \tag{3}$$

The functional form for the expansion coefficient is chosen to be the same as for the heat capacity:

$$\alpha(T, p_0) = \frac{\alpha_1 T^5 + \alpha_2 T^3}{T^4 + \alpha_3 T^2 + \alpha_4} = \frac{1}{v}\frac{\partial v}{\partial T} \tag{4}$$

The constants α_1, α_2, α_3, and α_4 have been fitted to data of Manzhelii et al.[4] For convenience we write the integral of α as

$$f_\alpha(T) = \int_{T_0}^{T} \alpha(T, p_0)\,\mathrm{d}T \tag{5}$$

For the partial derivative of the molar volume with respect to pressure consider the following form:

$$\frac{\partial v}{\partial p} = -\frac{A}{n}(Ap + B)^{-(n+1)/n}(K_1 T^2 + K_2 T + K_3) \tag{6}$$

The first pressure-dependent part ensures that the compressibility decreases with an increase of pressure, and the temperature-dependent part ensures that the compressibility increases with an increase of temperature. For convenience the temperature-dependent part will further be referred to as

$$K(T) = K_1 T^2 + K_2 T + K_3 \tag{7}$$

The constants A, B, n, K_1, K_2, and K_3 were fitted to isothermal compressibility data of Manzhelii et al.[4] and to data for the pressure dependence of the molar volume of Olinger[5] and Liu[6] at a temperature of about 296 K.

Combining eqs 2 to 6 with eq 1 and reducing the resulting equation by the reference temperature T_0 and the universal gas constant R = 8.314472 J·mol^{-1}·K^{-1} leads to the Gibbs free energy for dry ice in the following form:

$$\begin{aligned}\frac{g}{RT_0} &= g_0 + g_1\Delta\vartheta + g_2\Delta\vartheta^2\\ &+ g_3\left\{\ln\left(\frac{\vartheta^2 + g_4^2}{1 + g_4^2}\right) - \frac{2\vartheta}{g_4}\left[\arctan\left(\frac{\vartheta}{g_4}\right) - \arctan\left(\frac{1}{g_4}\right)\right]\right\}\\ &+ g_5\left\{\ln\left(\frac{\vartheta^2 + g_6^2}{1 + g_6^2}\right) - \frac{2\vartheta}{g_6}\left[\arctan\left(\frac{\vartheta}{g_6}\right) - \arctan\left(\frac{1}{g_6}\right)\right]\right\}\\ &\quad + g_7\Delta\pi[e^{f_\alpha(\vartheta)} + K(\vartheta)g_8] + g_9K(\vartheta)[(\pi + g_{10})^{(n-1)/n}\\ &\quad - (1 + g_{10})^{(n-1)/n}]\end{aligned} \tag{8}$$

The temperature T and the pressure p are replaced by the reduced temperature ϑ and the reduced pressure π. It is:

$$\vartheta = \frac{T}{T_0}, \qquad \Delta\vartheta = \vartheta - 1, \qquad \pi = \frac{p}{p_0}, \qquad \Delta\pi = \pi - 1 \tag{9}$$

The reference state has been set to

$$T_0 = 150\ \mathrm{K}, \qquad p_0 = 101325\ \mathrm{Pa},$$
$$v_0 = 2.7186286 \cdot 10^{-5}\ \mathrm{m^3 \cdot mol^{-1}} \tag{10}$$

Table 1. Values for the Parameters of Equation 8

$g_0 = -2.6385478 \cdot 10^0$	$g_0^\alpha = 3.9993365 \cdot 10^{-2}$
$g_1 = 4.5088732 \cdot 10^0$	$g_1^\alpha = 2.3945101 \cdot 10^{-3}$
$g_2 = -2.0109135 \cdot 10^0$	$g_2^\alpha = 3.2839467 \cdot 10^{-1}$
$g_3 = -2.7976237 \cdot 10^0$	$g_3^\alpha = 5.7918471 \cdot 10^{-2}$
$g_4 = 2.6427834 \cdot 10^{-1}$	$g_4^\alpha = 2.3945101 \cdot 10^{-3}$
$g_5 = 3.8259935 \cdot 10^0$	$g_5^\alpha = -2.6531689 \cdot 10^{-3}$
$g_6 = 3.1711996 \cdot 10^{-1}$	$g_6^\alpha = 1.6419734 \cdot 10^{-1}$
$g_7 = 2.2087195 \cdot 10^{-3}$	$g_7^\alpha = 1.7594802 \cdot 10^{-1}$
$g_8 = -1.1289668 \cdot 10^0$	$g_8^\alpha = 2.6531689 \cdot 10^{-3}$
$g_9 = 9.2923982 \cdot 10^{-3}$	$g_0^\kappa = 2.2690751 \cdot 10^{-1}$
$g_{10} = 3.3914617 \cdot 10^3$	$g_1^\kappa = -7.5019750 \cdot 10^{-2}$
$n = 7$	$g_2^\kappa = 2.6442913 \cdot 10^{-1}$

Table 2. Relation of Thermodynamic Properties to Equation 8 and Its Partial Derivatives

thermodynamic property	relation to g	
volume	$v = \frac{\partial g}{\partial p}$	(11)
entropy	$s = -\frac{\partial g}{\partial T}$	(12)
enthalpy	$h = g - T\frac{\partial g}{\partial T}$	(13)
internal energy	$u = g - T\frac{\partial g}{\partial T} - p\frac{\partial g}{\partial p}$	(14)
Helmholtz energy	$f = g - p\frac{\partial g}{\partial p}$	(15)
isochoric heat capacity	$c_p = -T\frac{\partial^2 g}{\partial T^2}$	(16)
cubic expansion coefficient	$\alpha = \left(\frac{\partial^2 g}{\partial T \partial p}\right) / \left(\frac{\partial g}{\partial p}\right)$	(17)
isothermal compressibility	$\kappa = -\left(\frac{\partial^2 g}{\partial p^2}\right) / \left(\frac{\partial g}{\partial p}\right)$	(18)

The coefficients g_2 to g_6 result from the integration of c_p, and the coefficients g_7 to g_{10} result from the integration of the thermal equation of state. g_0 and g_1 are integration constants and may be used to link eq 8 to the equation of state for the fluid phase. Hence g_0 and g_1 may be calculated according to the following relations:

$$g^{\mathrm{sol}}(T_{\mathrm{tr}}, p_{\mathrm{tr}}) = g^{\mathrm{vap}}(T_{\mathrm{tr}}, p_{\mathrm{tr}}) = g^{\mathrm{liq}}(T_{\mathrm{tr}}, p_{\mathrm{tr}}) \tag{19}$$

$$s^{\mathrm{sol}}(T_{\mathrm{tr}}, p_{\mathrm{tr}}) = s^{\mathrm{liq}}(T_{\mathrm{tr}}, p_{\mathrm{tr}}) - \frac{\Delta h^{\mathrm{melt}}}{T_{\mathrm{tr}}} \tag{20}$$

Δh^{melt} is the melting enthalpy at the triple point, and s is the molar entropy of the indicated phase. The melting enthalpy was measured by Kuehnen and Robson[7] and Maass and Barnes[8] and may be found in the Gas Encyclopædia of Air Liquide.[9] The value used in this work was treated as an adjustable parameter and has been set to Δh^{melt} = 8875 J·mol^{-1}. According to Span and Wagner[10] the temperature and pressure at the triple point is set to T_{tr} = 216.592 K and p_{tr} = 517950 Pa.

Table 3. Partial Derivatives of Equation 8 with Respect to Temperature and Pressure

equations for the derivatives of the Gibbs energy
$\frac{\partial g}{\partial T} = R\left\{g_1 + g_2 2\Delta\vartheta - \frac{2g_3}{g_4}\left[\arctan\left(\frac{\vartheta}{g_4}\right) - \arctan\left(\frac{1}{g_4}\right)\right] - \frac{2g_5}{g_6}\left[\arctan\left(\frac{\vartheta}{g_6}\right) - \arctan\left(\frac{1}{g_6}\right)\right] + g_7\Delta\pi\left[\exp(f_\alpha(\vartheta))\frac{\partial f_\alpha(\vartheta)}{\partial\vartheta} + g_8\frac{\partial K(\vartheta)}{\partial\vartheta}\right] + g_9\frac{\partial K(\vartheta)}{\partial\vartheta}[(\pi + g_{10})^{(n-1)/n} - (1 + g_{10})^{(n-1)/n}]\right\}$
$\frac{\partial g}{\partial p} = \frac{RT_0}{p_0}\left\{g_7[\exp(f^\alpha(\vartheta)) + g_8K(\vartheta)] + g_9K(\vartheta)\frac{n-1}{n}(\pi + g_{10})^{-1/n}\right\}$
$\frac{\partial^2 g}{\partial T\partial p} = \frac{R}{p_0}\left\{g_7\left[\exp(f^\alpha(\vartheta))\frac{\partial f^\alpha(\vartheta)}{\partial\vartheta} + g_8\frac{\partial K(\vartheta)}{\partial\vartheta}\right] + g_9\frac{\partial K(\vartheta)}{\partial\vartheta}\frac{n-1}{n}(\pi + g_{10})^{-1/n}\right\}$
$\frac{\partial^2 g}{\partial T^2} = \frac{R}{T_0}\left\{2g_2 - \frac{2g_3}{\vartheta^2 + g_4{}^2} - \frac{2g_5}{\vartheta^2 + g_6{}^2} + g_7\Delta\pi\left[\exp(f_\alpha(\vartheta))\frac{\partial^2 f_\alpha(\vartheta)}{\partial\vartheta^2} + \exp(f_\alpha(\vartheta))\left(\frac{\partial f_\alpha(\vartheta)}{\partial\vartheta}\right)^2 + g_8\frac{\partial^2 K(\vartheta)}{\partial\vartheta^2}\right] + g_9\frac{\partial^2 K(\vartheta)}{\partial\vartheta^2}[(\pi + g_{10})^{(n-1)/n} - (1 + g_{10})^{(n-1)/n}]\right\}$
$\frac{\partial^2 g}{\partial p^2} = \frac{RT_0}{p_0{}^2}\left\{g_9K(\vartheta)\frac{1-n}{n^2}(\pi + g_{10})^{-(n+1)/n}\right\}$

Table 4. Partial Derivatives of K and f_α with Respect to Temperature and Pressure

equation for the derivatives of K and f_α
$\frac{\partial K(\vartheta)}{\partial\vartheta} = 2g_0^\kappa\vartheta + g_1^\kappa$
$\frac{\partial^2 K(\vartheta)}{\partial\vartheta^2} = 2g_0^\kappa$
$\frac{\partial f_\alpha(\vartheta)}{\partial\vartheta} = 2g_0^\alpha\vartheta + g_1^\alpha\frac{2\vartheta - g_2^\alpha}{\vartheta^2 - g_2^\alpha\vartheta + g_3^\alpha} + g_4^\alpha\frac{2\vartheta + g_2^\alpha}{\vartheta^2 + g_2^\alpha\vartheta + g_3^\alpha} + \frac{g_5^\alpha}{g_7^\alpha}\frac{1}{1 + \left(\frac{\vartheta - g_6^\alpha}{g_7^\alpha}\right)^2} + \frac{g_8^\alpha}{g_7^\alpha}\frac{1}{1 + \left(\frac{\vartheta + g_6^\alpha}{g_7^\alpha}\right)^2}$
$\frac{\partial^2 f_\alpha(\vartheta)}{\partial\vartheta^2} = 2g_0^\alpha + g_1^\alpha\frac{2(\vartheta^2 - g_2^\alpha\vartheta + g_3^\alpha) - (2\vartheta - g_2^\alpha)^2}{(\vartheta^2 - g_2^\alpha\vartheta + g_3^\alpha)^2} + g_4^\alpha\frac{2(\vartheta^2 + g_2^\alpha\vartheta + g_3^\alpha) - (2\vartheta + g_2^\alpha)^2}{(\vartheta^2 + g_2^\alpha\vartheta + g_3^\alpha)^2} - \frac{g_5^\alpha}{(g_7^\alpha)^2}\frac{1}{\left(1 + \left(\frac{\vartheta - g_6^\alpha}{g_7^\alpha}\right)^2\right)^2}2\frac{\vartheta - g_6^\alpha}{g_7^\alpha} - \frac{g_8^\alpha}{(g_7^\alpha)^2}\frac{1}{\left(1 + \left(\frac{\vartheta + g_6^\alpha}{g_7^\alpha}\right)^2\right)^2}2\frac{\vartheta + g_6^\alpha}{g_7^\alpha}$

Finally combining eqs 4, 5, and 10 yields:

$$f_\alpha(\vartheta) = g_0^\alpha(\vartheta^2 - 1) + g_1^\alpha \ln\left(\frac{\vartheta^2 - g_2^\alpha\vartheta + g_3^\alpha}{1 - g_2^\alpha + g_3^\alpha}\right) + g_4^\alpha \ln\left(\frac{\vartheta^2 + g_2^\alpha\vartheta + g_3^\alpha}{1 + g_2^\alpha + g_3^\alpha}\right) + g_5^\alpha\left[\arctan\left(\frac{\vartheta - g_6^\alpha}{g_7^\alpha}\right) - \arctan\left(\frac{1 - g_6^\alpha}{g_7^\alpha}\right)\right] + g_8^\alpha\left[\arctan\left(\frac{\vartheta + g_6^\alpha}{g_7^\alpha}\right) - \arctan\left(\frac{1 + g_6^\alpha}{g_7^\alpha}\right)\right] \quad (21)$$

Replacing the temperature in eq 7 by the reduced temperature leads to:

$$K(\vartheta) = g_0^\kappa\vartheta^2 + g_1^\kappa\vartheta + g_2^\kappa \quad (22)$$

Values for all constants of eq 8, 21, and 22 are listed in Table 1. g_0 and g_1 have been chosen such that the equation for dry ice has the same reference point as the reference equation for CO_2 in the fluid phase by Span and Wagner.[10]

RESULTS AND DISCUSSION

To analyze the behavior of eq 8 we examined the deviations between the measured thermodynamic properties and the properties calculated using the new fundamental equation of state. All thermodynamic properties of a substance can be calculated from a fundamental equation and its derivatives with respect to the independent variables on which the equation depends. Table 2 gives a brief overview of the partial derivatives used to calculate thermodynamic properties from eq 8. The respectively needed derivatives are given in Table 3. The derivatives of K and f_α are given in Table 4. Numerical values at different temperatures and pressures are provided in Table 5.

In Figure 1 the relative deviation of calculated heat capacity data from experimental values is plotted over temperature. All of the data were measured along the sublimation curve, so the corresponding pressure to each temperature is the respective

Table 5. Numerical Check Values

	$T = T_{tr} = 216.592$ K	$T = 100$ K
thermodynamic property	$p = p_{tr} = 0.51795$ MPa	$p = 100$ MPa
$g/(\mathrm{J \cdot mol^{-1}})$	$-1.447007522 \cdot 10^{3}$	$-2.961795962 \cdot 10^{3}$
$v/(\mathrm{m^3 \cdot mol^{-1}})$	$2.848595255 \cdot 10^{-5}$	$2.614596591 \cdot 10^{-5}$
$s/(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	$-1.803247012 \cdot 10^{1}$	$-5.623154438 \cdot 10^{1}$
$c_p/(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	$5.913420271 \cdot 10^{1}$	$3.911045710 \cdot 10^{1}$
$\alpha/(\mathrm{K^{-1}})$	$8.127788321 \cdot 10^{-4}$	$3.843376525 \cdot 10^{-4}$
$\kappa/(\mathrm{Pa^{-1}})$	$2.813585169 \cdot 10^{-10}$	$1.149061787 \cdot 10^{-10}$

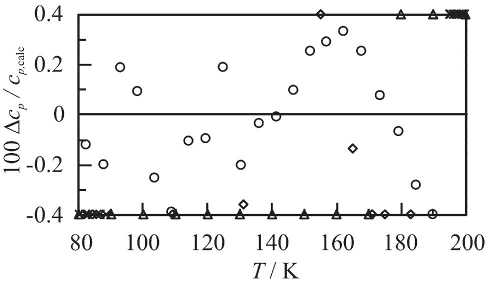

Figure 1. Relative deviations $100\Delta c_p/c_{p,\mathrm{calc}} = 100(c_{p,\mathrm{calc}} - c_{p,\mathrm{exp}})/c_{p,\mathrm{calc}}$ of heat capacity data from values calculated from eq 16. ×, Eucken;[12] △, Eucken and Hauck;[11] ○, Giauque and Egan;[3] ◇, Maass and Barnes.[8]

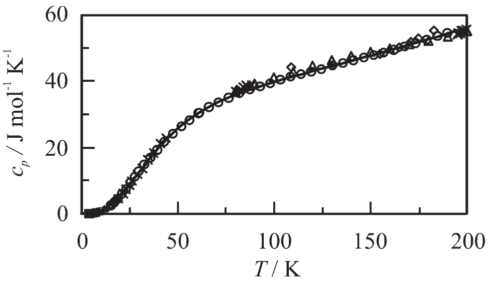

Figure 2. Isobaric heat capacity: experimental data and values calculated from eq 16. —, calculated; ×, Eucken;[12] △, Eucken and Hauck;[11] ○, Giauque and Egan;[3] ◇, Maass and Barnes;[8] +, Manzhelii et al.[4]

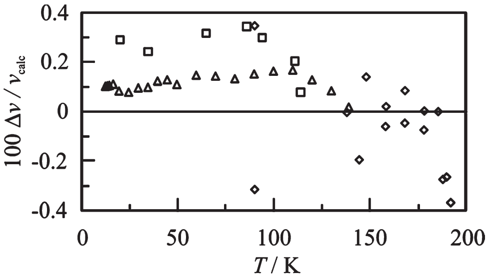

Figure 3. Relative deviations $100\Delta v/v_{\mathrm{calc}} = 100(v_{\mathrm{calc}} - v_{\mathrm{exp}})/v_{\mathrm{calc}}$ of molar volume data from values calculated from eq 11. ◇, Maass and Barnes;[8] △, Manzhelii et al.;[4] □, Keesom and Köhler.[14]

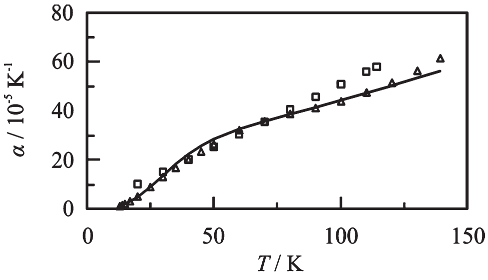

Figure 4. Thermal expansion coefficient α: data and values calculated from eq 17. —, calculated; □, Keesom and Köhler;[14] △, Manzhelii et al.[4]

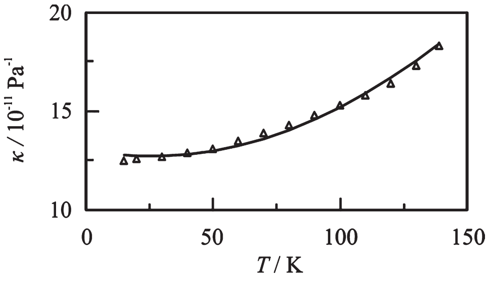

Figure 5. Compressibility κ: data and values calculated from eq 18. —, calculated; △, Manzhelii et al.[4]

sublimation pressure. Equation 2 was only fitted to the data of Giauque and Egan,[3] who state an experimental uncertainty of 0.2 % for temperatures between (35 and 195) K. As seen in Figure 1 the maximum deviation does not exceed 0.4 %. But the deviation of some heat capacities calculated from eq 8 from the experimental data of Giauque and Egan[3] exceeds the experimental uncertainty. Concerning the year the data were measured and taking a closer look at it, we think Giauque and Egan[3] might have underestimated their uncertainties slightly. Nevertheless, compared to data of other authors, the data of Giauque and Egan[3] are the most accurate for temperatures greater than 80 K. Eucken and Hauck[11] state an uncertainty of 1.5 %; the other authors do not give information about their estimated measurement uncertainties. Heat capacities for temperatures lower than 80 K were not only measured by Giauque and Egan[3] but also by Eucken[11] and Manzhelii et al.[4] as displayed in Figure 2.

In Figure 3 relative deviations of molar volume data from calculated values are plotted over temperature. Again the corresponding pressure is the sublimation pressure. The most accurate measurements are considered to be those of Manzhelii et al.[4] The deviations of calculated values from the experimental data by Manzhelii et al.[4] do not exceed 0.2 %. Deviations from experimental data by Keesom and Köhler[14] and Maass and Barnes[8] do not exceed 0.4 %, respectively.

In Figure 4 thermal expansion coefficient data and calculated values from eq 17 and in Figure 5 isothermal compressibility data and values calculated from eq 18 are plotted over temperature. Again the pressure corresponds to the sublimation pressure. In setting up the equation, one of the assumptions we had to make was that, at a constant temperature for 0 MPa to p_{tr} c_p, α and κ are constant. To assess the impact of these assumptions we analyzed relative deviations of these properties for temperatures between 80 K and T_{tr} and pressures between 0 MPa and p_{tr}. The maximum deviation for the heat capacity was found at T_{tr} and is $(c_p(T_{tr}, 0\,\mathrm{MPa}) - c_p(T_{tr}, p_{tr}))/c_p(T_{tr}, p_{tr}) = 0.02$ %. The maximum

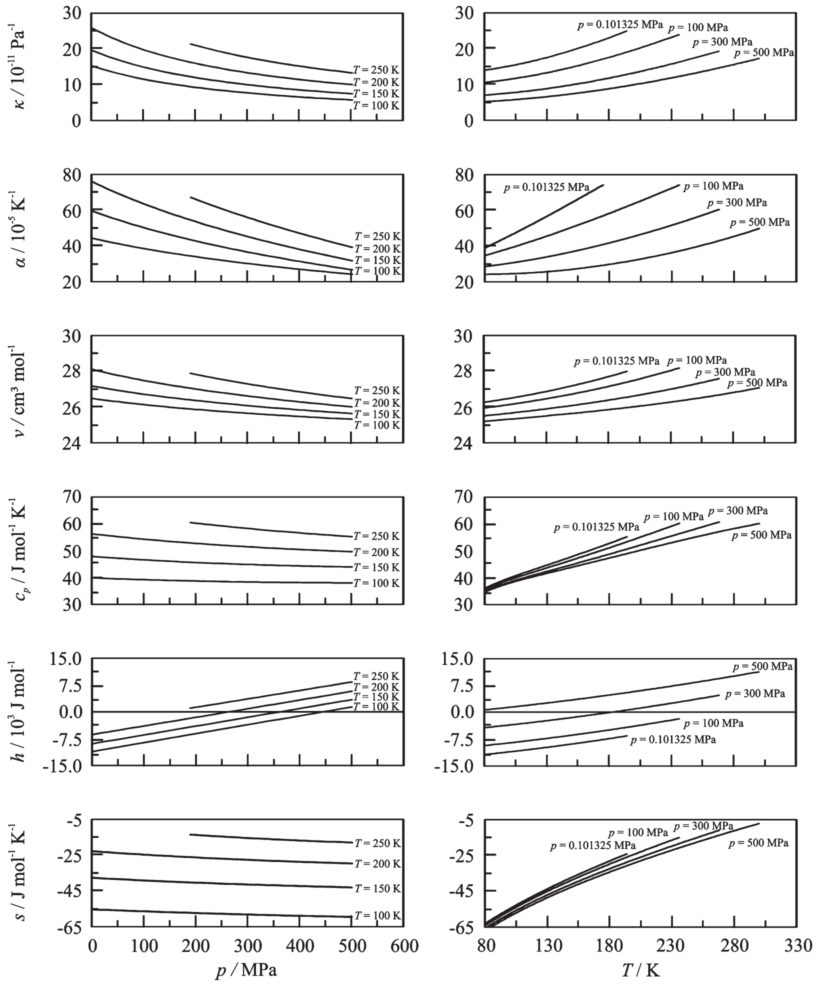

Figure 6. Isobars and isotherms for some properties calculated from eq 8 and its derivatives.

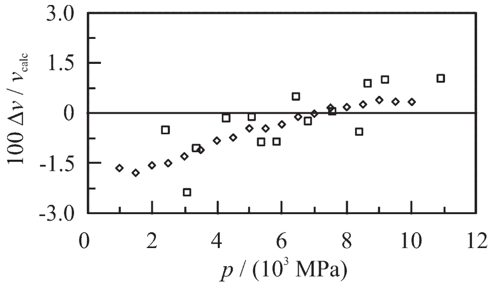

Figure 7. Relative deviations $100\Delta v/v_{\text{calc}} = 100(v_{\text{calc}} - v_{\text{exp}})/v_{\text{calc}}$ of molar volume data from calculated values from eq 11. □, Liu;[6] ◇, Olinger.[5]

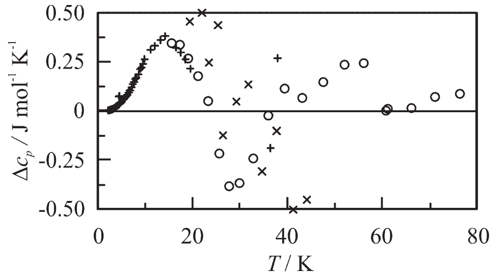

Figure 8. Deviations $\Delta c_p = c_{p,\text{calc}} - c_{p,\text{exp}}$ of low temperature heat capacity data from values calculated from eq 16. ×, Eucken;[12] ○, Giauque and Egan;[3] +, Manzhelii et al.[4]

deviation for κ was found to be 0.165 % and for α 0.096 %. These deviations are small compared to deviations from the measured values available; the initial assumptions are justified.

Range of Validity and Extrapolation Behavior. To use the dry ice equation for phase equilibrium calculations eq 8 has to cover a wide range of pressures and temperatures, for which no experimental data are available. Thus, it has to be proven that eq 8 behaves qualitatively correctly within a sufficiently large range of validity. For demonstration purposes isobars and isotherms for some thermodynamic properties are plotted over temperature in Figure 6. Equation 8 shows reasonable physical behavior up to pressures of about 500 MPa. The lower temperature limit has been set to 80 K since for very low temperatures physically incorrect solutions may occur. Thus the range of validity for eq 8 has been set to 0 MPa < p < 500 MPa and 80 K < T < 300 K. The upper temperature limit corresponds to a melting pressure of about 500 MPa.

For some thermal properties experimental data are available outside the range of validity; extrapolation of these properties yields good results. The high-pressure molar volume data of Olinger[5] and Liu[6] are reproduced with a maximum deviation of about 2 % (Figure 7) and the deviation from experimental data for

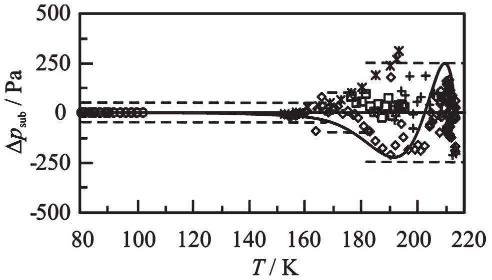

Figure 9. Deviations $\Delta p_{\text{sub}} = p_{\text{sub,corr.eq}} - p_{\text{sub,calc(exp)}}$ of sublimation pressures calculated from the phase equilibrium condition from values calculated from the correlation equation by Span and Wagner.[10] The fundamental equation by Span and Wagner[10] was used for the gas phase. —, calculated; – –, uncertainty; □, Ambrose;[18] △, Bedford et al.;[15] ◇, Bilkadi et al.;[16] ○, Bryson et al.;[17] +, Fernandez-Fassnacht and del Rio;[19] *, Giauque and Egan.[3]

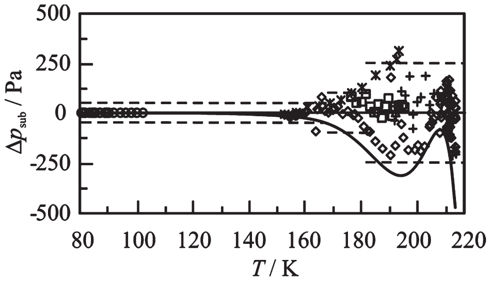

Figure 10. Deviations $\Delta p_{\text{sub}} = p_{\text{sub,corr.eq}} - p_{\text{sub,calc(exp)}}$ of sublimation pressures calculated from the phase equilibrium condition from values calculated from the correlation equation by Span and Wagner.[10] The fundamental equation by Ely et al.[20] was used for the gas phase. —, calculated; – –, uncertainty; □, Ambrose;[18] △, Bedford et al.;[15] ◇, Bilkadi et al.;[16] ○, Bryson et al.;[17] +, Fernandez-Fassnacht and del Rio;[19] *, Giauque and Egan.[3]

extrapolation of c_p to temperatures lower than 80 K does not exceed 0.4 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ as shown in Figure 8. The thermal expansion coefficient and the isothermal compressibility may be extrapolated to lower temperatures too (for pressures up to the triple point pressure) as seen before in Figures 4 and 5. It can be seen from Figure 3 that extrapolation to temperatures lower than 80 K for the molar volume at pressures up to the triple point pressure also gives good results.

Sublimation Pressure. Sublimation pressures of CO_2 have been measured by Bedford et al.,[15] Bilkadi et al.,[16] Bryson et al.,[17] Ambrose,[18] Giauque and Egan,[3] and Fernandez-Fassnacht and del Rio.[19] Span and Wagner[10] established an accurate correlation equation for the sublimation pressure, based on selected experimental data. They state that the uncertainty of their equation is $\Delta p_{\text{sub}} \leq \pm 250$ Pa for 185 K $\leq T \leq T_{\text{tr}}$, $\Delta p_{\text{sub}} \leq \pm 100$ Pa for 170 K $\leq T \leq$ 185 K, and $\Delta p_{\text{sub}} \leq \pm 50$ Pa for $T \leq$ 170 K. Equation 8 allows for equilibrium pressure calculations by finding pressures p and temperatures T, which satisfy the phase equilibrium condition for pure substances:

$$\mu^{\text{sol}}(T,p) = \mu^{\text{vap}}(T,p) \Leftrightarrow g^{\text{sol}}(T,p) = g^{\text{vap}}(T,p) \tag{23}$$

Since eq 23 cannot be solved analytically, we have to find a solution numerically setting the break condition to

$$\left| g^{\text{sol}}(T,p) - g^{\text{vap}}(T,p) \right| < 0.000001\ \text{J}\cdot\text{mol}^{-1} \tag{24}$$

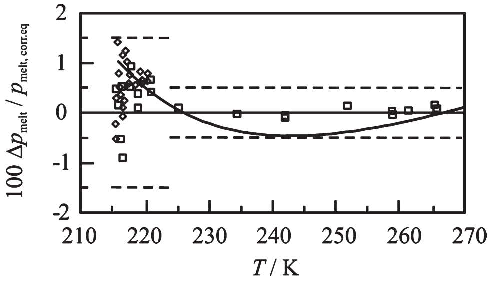

Figure 11. Relative deviations $100\Delta p_{\text{melt}}/p_{\text{melt,corr.eq}} = 100(p_{\text{melt,corr.eq}} - p_{\text{melt,calc(exp)}})/p_{\text{melt,corr.eq}}$ of melting pressures calculated from the phase equilibrium condition from values calculated from the correlation equation by Span and Wagner.[10] The fundamental equation by Span and Wagner[10] was used for the fluid phase. —, calculated; – –, uncertainty; ◇, Clusius et al.;[22] □, Michels et al.[21]

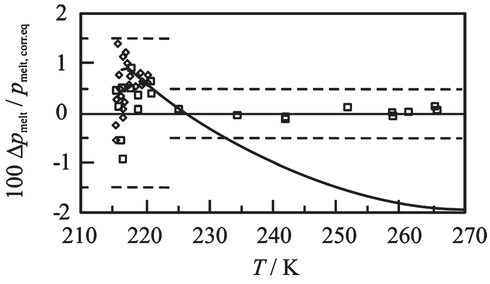

Figure 12. Relative deviations $100\Delta p_{\text{melt}}/p_{\text{melt,corr.eq}} = 100(p_{\text{melt,corr.eq.}} - p_{\text{melt,calc(exp)}})/p_{\text{melt,corr.eq}}$ of melting pressures calculated from the phase equilibrium condition from values calculated from the correlation equation by Span and Wagner.[10] The fundamental equation by Ely et al.[20] was used for the fluid phase. —, calculated; – –, uncertainty; ◇, Clusius et al.;[22] □, Michels et al.[21]

In Figure 9 deviations of the correlation equation from experimental values and values calculated using eq 8 for the solid phase and the reference equation for carbon dioxide by Span and Wagner[10] for the gas phase are presented. Additionally the uncertainties of the correlation equation given by Span and Wagner[10] are shown.

Ideally, the calculated sublimation pressures, which are indicated by the solid line, should stay within the uncertainty of the correlation equation. The results do not quite meet this requirement, and some calculated values deviate slightly more than the uncertainty of the correlation equation. We studied this effect by using another equation of state for the gas phase. Employing the also highly accurate equation by Ely et al.[20] required some modification of eq 8 regarding the constants g_0 and g_1 since both the entropy of the liquid at the triple point (see eq 20) and the Gibbs free energy of the vapor and liquid phases at the triple point (see eq 19) change. After recalculation of the constants the phase equilibrium condition remains the same. The results obtained by using the equation of state by Ely et al.[20] instead of the equation by Span and Wagner[10] are shown in Figure 10.

The calculated sublimation pressures depend significantly on the equation used for the fluid phase. Furthermore small differences in the Gibbs energy for either the fluid or the solid phase lead to significant changes in calculated sublimation pressures. Considering this, better results for sublimation pressure calculation could only be achieved by either fitting the equation for the solid or fitting the equation for the fluid phase to the sublimation

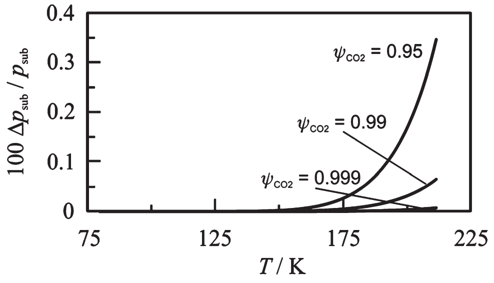

Figure 13. Relative deviations $100\Delta p_{sub}/p_{sub} = 100(p_{sub} - p_{sub,ideal})/p_{sub}$ in sublimation pressures for three different mixtures of CO_2 with N_2. The deviation of calculated sublimation pressures according to eq 26 from pressures calculated from eq 28 is plotted over temperature.

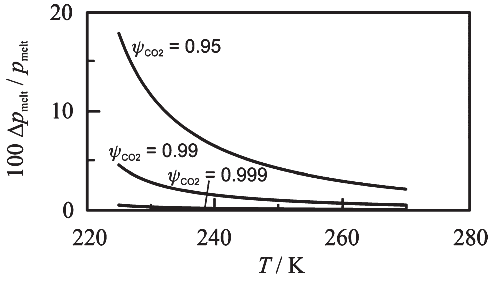

Figure 14. Relative deviations $100\Delta p_{melt}/p_{melt} = 100(p_{melt} - p_{melt,ideal})/p_{melt}$ in melting pressures for three different mixtures of CO_2 with N_2. The deviation of calculated melting pressures according to eq 27 from pressures calculated from eq 29 is plotted over temperature.

pressure data. So far phase equilibrium calculations are predictive—neither of the two equations of state was fitted to sublimation pressures.

Melting Pressure. Melting pressures of CO_2 have been measured by Michels et al.[21] and Clusius et al.[22] Span and Wagner[10] also established an accurate correlation equation for the melting pressure of CO_2. They estimated the uncertainty of this equation to be $\Delta p_{melt}/p_{melt} \leq \pm 1.5$ % for $T_{tr} \leq T \leq 225$ K and $\Delta p_{melt}/p_{melt} \leq \pm 0.5$ % for 225 K $\leq T \leq$ 270 K. The phase equilibrium condition for the solid and the liquid phase remains the same as for the sublimation equilibrium. So eq 23 may be rewritten:

$$\mu^{sol}(T, p) = \mu^{liq}(T, p) \Leftrightarrow g^{sol}(T, p) = g^{liq}(T, p) \qquad (25)$$

Again, the phase equilibrium condition has to be solved iteratively. The relative deviations of the correlation equation from experimental data as well as from the melting pressures calculated using eq 8 and the reference equation for carbon dioxide by Span and Wagner[10] are presented in Figure 11. The deviations of the calculated pressures from the correlation equation from the pressures calculated using eq 8 stay within the uncertainty stated by Span and Wagner[10] throughout the whole temperature range for which the correlation equation is valid. For comparison, the equation of state for the fluid phase by Ely et al.[20] was used to calculate equilibrium pressures in Figure 12. The melting pressures calculated this way deviate significantly from the correlation equation, but this result was to be expected since the Helmholtz equation by Ely et al.[20] is valid only for pressures up to 100 MPa (the corresponding melting temperature is about 236 K). Nevertheless it can be stated that calculated melting pressures are rather sensitive to the representation of Gibbs energies in the liquid phase.

Equilibrium Pressures for Mixtures. Additionally we studied the effect of small impurities (N_2) in the CO_2 on the equilibrium pressures. Therefore we chose three different mixtures (ψ_{CO_2} = 0.95, ψ_{N_2} = 0.05; ψ_{CO_2} = 0.99, ψ_{N_2} = 0.01; ψ_{CO_2} = 0.999, ψ_{N_2} = 0.001) and calculated the sublimation pressure according to

$$\mu^{sol}(T, p) = \mu^{vap}_{CO_2}(T, p, \psi) \Leftrightarrow g^{sol}(T, p) = \mu^{vap}_{CO_2}(T, p, \psi) \qquad (26)$$

This simple equilibrium condition is valid if the solid phase consists only of CO_2 (dry ice). The melting pressure was calculated according to

$$\mu^{sol}(T, p) = \mu^{liq}_{CO_2}(T, p, \psi) \Leftrightarrow g^{sol}(T, p) = \mu^{liq}_{CO_2}(T, p, \psi) \qquad (27)$$

The equations used were again the reference equation for CO_2 by Span and Wagner[10] and for N_2 the reference equation by Span et al.[23] was used. The mixing rule was taken from the GERG 2004 equation of state for natural gases by Kunz et al.[24] The solid phase is assumed to be pure dry ice. These pressures are compared to the ideally calculated equilibrium pressures according to eqs 28 and 29.

$$p^{sub}(T, \psi) = \frac{p^{sub}_{pure\,CO_2}(T)}{\psi_{CO_2}} \qquad (28)$$

$$p^{melt}(T, \psi) = \frac{p^{melt}_{pure\,CO_2}(T)}{\psi_{CO_2}} \qquad (29)$$

The relative deviations of the calculated pressures using the new equation for dry ice and the ideal pressures are shown in Figures 13 and 14.

The deviations of the ideally calculated sublimation pressures from calculated values (Figure 13) increase as the temperature increases and with increasing N_2 concentration. This is somewhat expected since with the increase of temperature (and by that the increase of the sublimation pressure) and with increasing N_2 concentration the assumption of an ideal mixture gets worse. The relative deviations for the melting pressure (Figure 14) also increase with the amount of N_2 in the mixture but decrease with increasing temperature. In the liquid phase the deviations of the ideally calculated melting pressures from the calculated ones are much higher than those in the gas phase. The reasons are that the ideal mixture model does not work well for liquids and that the N_2 concentration has a large contribution to g of the mixture.

■ CONCLUSIONS AND PERSPECTIVE

A new equation of state for solid carbon dioxide based on the Gibbs free energy has been developed; the range of validity was set to 0 MPa < p < 500 MPa and 80 K < T < 300 K. Most of the available thermodynamic property data are represented within the uncertainty of the experimental data. For temperatures and pressures within the range of validity eq 8 ensures physically correct behavior. In combination with a fundamental equation for the fluid phase of carbon dioxide, the equation for the solid allows for accurate calculation of phase equilibrium pressures. Therefore this equation might be used for more complex phase equilibrium calculation, for example, flash calculations or phase equilibria including mixtures as demonstrated in this work. Further improvement of this equation may require another structure of the equation and another fitting procedure, where the equilibrium data is also taken into account. Therefore the next step would be to think about a general form for the Gibbs free energy of solids and fit this equation and its derivatives to the experimental data, like it is done for fundamental equations of state for the fluid phase.

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