Prediction of some thermophysical properties of SF_6 at low pressure

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Abstract. In this paper, some thermophysical properties at low pressure of sulphur hexafluoride (SF_6) fluid are modelled and predicted. Also, by comparing the obtained results with experimental data, the correlation performance of virial coefficients to predict thermodynamic properties over a wide temperature range is evaluated. Studied properties consist of Joule–Thomson coefficient, enthalpy, deviation function, fugacity coefficient, thermal expansion, Boyle temperature and Boyle volume. The studied correlation function is the one suggested by Zarkova *et al* and compared with correlation of Meng *et al*. The obtained results show that the correlation equation presented has a good ability to predict the thermophysical properties of sulpur hexafluoride and its deviation from the ideal state over a wide range of temperatures. Average absolute deviations (AAD) of thermophysical properties of SF_6 calculated by this approach is mainly below 5%.

1. Introduction

Sulphur hexafluoride (SF_6) was first prepared by Moissan by burning sulphur in an atmosphere of fluorine and removing the lower fluorides by pyrolysis at 400°C. This method is still used for commercial synthesis of SF_6, which is a colourless, odourless, tasteless, non-toxic and non-flammable gas under ordinary conditions. It is a greenhouse gas and has very low solubility in water. Sulphur hexafluoride deserves special attention because of its industrial applications. It exhibits excellent insulating properties for high voltage apparatus even at relatively low pressure and it is stable to silent electric discharge. SF_6 remains unchanged even at 500°C, which again demonstrates its unique inactivity. SF_6 is a highly stable, symmetrically shaped chemical compound which is widely used in several industrial applications [1]. Because of its thermophysical properties, mixture of SF_6 with argon or krypton can be used to improve the thermal insulation of double glazed windows and as an inert solvent for chemical reactions in supercritical fluids [2].

Due to many applications of SF_6 in industry, researchers have tried to determine its thermodynamic and physicochemical properties theoretically and experimentally. For many years, different potentials using different methods (such as *ab-initio* calculations and fitting procedures) have been proposed for SF_6 and its mixtures [3–8] and some simulations using different potentials were performed [9,10] and some equations of state proposed [2].

In [11], Joule–Thomson and deviation functions at low pressure were calculated for refrigerant fluids to evaluate the performance of their correlation equation at low pressure and wide range of temperature. It was shown that the accurate correlation equation presented had a very good ability to predict the thermophysical properties of materials and their deviation from the ideal state over a wide temperature range.

In this paper, we calculate some thermodynamic properties of SF_6 at low pressure using its virial coefficients. Till now, nobody has used this approach to calculate and model some of the thermophysical properties of this material.

2. Virial equation of state (VEOS)

Equations of state (EOSs) are important tools for predicting and modelling thermodynamic properties of

materials over a wide range of temperatures and pressures. Therefore, many publications deal with their development or improvement [12–14].

One of the oldest models for calculating the thermophysical properties of fluids is the virial equation of state (VEOS), which provides the required information with relatively good accuracy

$$Z = 1 + \sum_{n=2} B_n \rho^{n-1} \tag{1}$$

or

$$Z = 1 + \sum B_n^+ P^{n-1} \tag{2}$$

in which

$$B_2^+ = B_2/RT$$
$$B_3^+ = (B_3 - B_2^2)/R^2T^2. \tag{3}$$

It is better to consider here $B_2 \equiv B$ and $B_3 \equiv C$. In the above equations, Z is the compressibility factor ($Z = pV_m/RT$), ρ is the density ($\rho = 1/V_m$) and B_n is the nth virial coefficient. VEOS has a strong theoretical basis in statistical mechanics. In fact, the virial coefficients are related to intermolecular interactions by exact statistical-mechanical formulae. In this respect, nth virial coefficient is related to molecular interactions in clusters of n molecules. For example, the second coefficient indicates the interaction between a pair of molecules, the third coefficient indicates the interaction of three molecules in the cluster, and so on. Thus, the virial coefficient is the connection bridge between microscopic and macroscopic properties and show the non-ideal behaviour of real fluids [15]. From this view point, by accurately identifying the virial coefficients and how they depend on temperature and using VEOS, it is easy to calculate the thermodynamic properties of fluids.

Virial coefficients can be obtained using both experimental methods like PVT, speed of sound, Joule–Thomson measurements and theoretical approaches consisting of equations of state and interaction potential functions [15–27].

Most of the research on virial coefficients are made to obtain a general relationship for many molecules. In 1957, for the second virial coefficients of non-polar gases, Pitzer and Curl [28] presented a successful correlation. Then this correlation has been modified by O'Connell and Prausnitz [29], Tsonopoulos [30,31], Tarakad and Danner [32], Orbey [33], Weber [34], and Hayden and O'Connell [26] by refitting the coefficients of the Pitzer–Curl correlation, added polar and hydrogen bonding terms and applied new parameters. Also, Tian *et al*, using virial coefficients, have derived a new equation of state for hard sphere and polyhedron fluids with high accuracy [35–37].
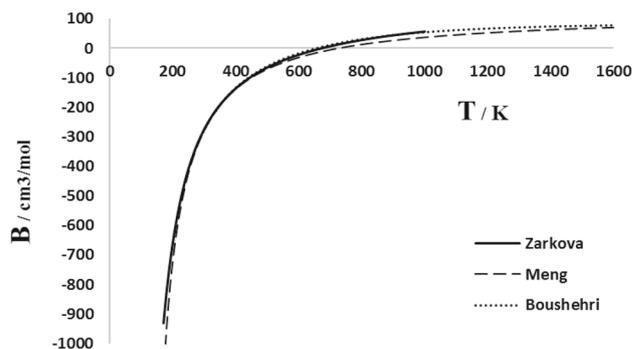
Figure 1. Three correlation functions of second virial coefficient for SF_6 vs. temperature.

In 1987, Boushehri *et al* presented the correlation function of second virial coefficient for linear molecules like N_2, near-linear molecules like C_2H_4 and near-spherical molecules like SF_6 [38]. In this regard, two restrictions were considered. First, it is restricted to the low-density calculation and second, the temperature range is restricted to $T^* > 1$, where $T^* = kT/\varepsilon$ and ε is the depth of the potential well.

In recent years, Zarkova and Hohm presented results on self-consistent calculations of second PVT–virial coefficients $B(T)$, viscosity data $\eta(T)$ and diffusion coefficients $\rho D(T)$ for eleven heavy globular gases like SF_6 [39]. Also, Meng *et al* have developed a modified form of Tsonopoulos correlation for second and third virial coefficients of pure fluids based on the corresponding state principle [16]. They showed that these calculations and their equations can predict the experimental data very well. In this respect, figure 1 compares the three correlation functions of second virial coefficient of SF_6 obtained by Zarakova (from 170 to 1000 K), Boushehri (from 260 to 2000 K) and Meng (it seems up to $4T_r$). As can be seen, at temperatures below 200 K and above 700 K, Zarkova and Meng's correlations are rather different but, correlations of Zarkova and Boushehri have an excellent match. However, in a wide range of temperatures (200 to 700 K), there is a very good match between the three correlation equations. Due to their compatibility in the mentioned temperature range, in this research work, a model for predicting the thermophysical properties of SF_6 is presented and by comparing the results with experimental data, the proposed model is evaluated.

In this paper, the thermophysical properties of SF_6 are predicted and modelled using Zarkova's correlation equation from 170 to 1000 K. This range is very suitable for model evaluation. In this regard, the changes in thermophysical properties resulting from the Meng's equation will also be discussed.

Zarkova's correlation for the second virial coefficient is as follows:

$$B(T) = d_1 + \frac{d_2}{T} + \frac{d_3}{T^2} + \frac{d_4}{T^3} = \sum_{n=1}^{4} \frac{d_n}{T^{n-1}} \qquad (4)$$

in which d_n are the expansion coefficients of the equation.

At low pressure or density, third terms of virial equation of state (eqs (2) and (3)) onwards can be ignored in the expansion and so we have

$$Z(T, \rho) = 1 + B(T)\rho$$

or

$$Z(T, P) = 1 + B^+(T)P. \qquad (5)$$

Therefore, using eq. (5) and having only the accurate second viral coefficient, many thermodynamic properties of fluids can be predicted and modelled.

What is considered in this research is the use of VEOS at low pressure and the second virial coefficient obtained from Zarkova's correlation equation to model some thermodynamic properties of SF_6. The use of virial coefficients to predict and model some of the thermophysical properties of SF_6, which is the subject of this research, has not been done before. In this regard and using eqs (4) and (5), we have

$$Z_{\text{Zarkova}} = 1 + \left(162.8 - \frac{1.053 \times 10^5}{T} \right.$$
$$\left. + \frac{1.1 \times 10^5}{T^2} - \frac{2.347 \times 10^9}{T^3} \right) \rho. \qquad (6)$$

In this work, some thermophysical properties of SF_6 at low pressure are calculated and modelled using eq. (6).

3. Thermophysical properties

In our work, we calculate the following thermophysical properties of SF_6 using the correlation function of virial coefficients.

3.1 *Joule–Thomson coefficient*

In thermodynamics, the Joule–Thomson (J–T) effect is related to temperature change of a fluid when that fluid is forced to pass through a valve or porous plug so that heat is not exchanged with the environment. The J–T effect is of considerable importance in refrigeration and gas liquefaction processes. In this regard, the J–T coefficient (μ_π) is defined as follows:

$$\mu_\pi = \left(\frac{\partial T}{\partial P} \right)_H = -\frac{1}{C_{p,m}} \left(\frac{\partial H}{\partial P} \right)_T \qquad (7)$$

in which $C_{P,m}$ is the heat capacity. This coefficient can be positive, negative or zero.

Joule–Thomson coefficient can be shown as the expansion by pressure in which expansion coefficients depend on virial coefficients as follows [11,40]:

$$\mu_\pi = \frac{1}{C_{P,m}} \sum_{n=0} A_n P^n = \frac{1}{C_{P,m}} (A_0 + A_1 P + \cdots)$$

$$A_0 = T \frac{dB}{dT} - B$$

$$A_1 = \frac{1}{R} \left(\frac{dC}{dT} - 2B \frac{dB}{dT} \right) + \frac{2}{RT} \left(B^2 - C \right). \qquad (8)$$

At zero pressure, we have

$$\mu_\pi^0(T) = \frac{A_0(T)}{C_{P,m}^0} = \frac{1}{C_{P,m}^0} \left(T \frac{dB(T)}{dT} - B(T) \right),$$

$$A_0(T) = \mu_\pi^0(T) C_{P,m}^0(T) = -\left(\frac{\partial H}{\partial P} \right)_T^0, \qquad (9)$$

where μ_π^0 and $C_{P,m}^0$ are the J–T coefficient and heat capacity at zero pressure respectively. Also, $(\partial H/\partial P)_T^0$ is the enthalpy changes relative to the pressure at zero pressure or at ideal conditions. In my previous paper, it was shown that zero pressure J–T coefficient can be written as follows [11]:

$$\mu_\pi^0(T) = \frac{1}{\left(1 + \frac{3}{2}N\right) R} \left(T \frac{dB(T)}{dT} - B(T) \right), \qquad (10)$$

where N is the number of atoms in a molecule. J–T coefficient of an ideal gas is zero, because there is no interaction between their molecules. However, eqs (8) and (10) show that J–T coefficient of real gas is not zero in the limit of zero pressure. In this regard, zero pressure J–T coefficient (μ_π^0) can be used as a measure of deviation from the ideal state due to the interactions related to the pair of molecules. These deviations can provide useful information about the nature of intermolecular forces.

3.2 *Deviation function*

As mentioned before, the virial coefficients are the connection bridge between microscopic and macroscopic properties and show the non-ideal behaviour of real fluids. Therefore, having virial coefficients, non-ideality measurement can be calculated using deviation functions in different pressures and temperatures. Based on the thermodynamic relations for the deviation function of enthalpy, we have

$$H_m^{id}(T, P) - H_m(T, P)$$
$$= \int_0^P \left[T \left(\frac{\partial V_m}{\partial T} \right)_P - V_m \right] dP. \tag{11}$$

Deviation functions, the same as J–T coefficient, can be written as the expansion by pressure in which expansion coefficients depend on virial coefficients as follows [11, 40]:

$$H_m^{id}(T, P) - H_m(T, P) = \sum_{n=1} b_n P^n$$

$$b_1 = A_0 = T \frac{dB}{dT} - B$$

$$b_2 = \frac{1}{2} A_1 = \frac{1}{2R} \left(\frac{dC}{dT} - 2B \frac{dB}{dT} \right) + \frac{1}{RT} \left(B^2 - C \right). \tag{12}$$

It is clear that deviation functions aref equal to zero when $P = 0$ and of course, at low pressure, second terms onwards can be ignored in the expansion.

3.3 *Fugacity coefficient*

In chemical thermodynamics, the fugacity of a real gas is the effective partial pressure which replaces the mechanical partial pressure in an accurate computation of the chemical equilibrium constant. The real gas pressure and fugacity are related through the dimensionless fugacity coefficient φ

$$\frac{f}{p} = \varphi. \tag{13}$$

For an ideal gas, fugacity and pressure are equal and so $\varphi = 1$. Taken at the same temperature and pressure, the difference between the molar Gibbs free energies of a real gas and the corresponding ideal gas is equal to $RT \ln \varphi$. In this relation, fugacity coefficient φ can be calculated as
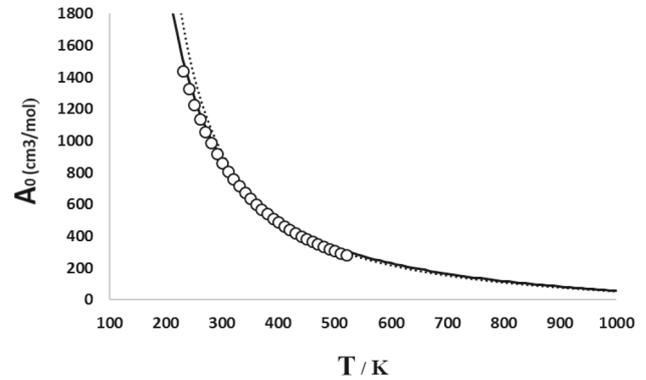
$$\ln \varphi = \int_0^p \left(\frac{Z - 1}{p} \right) dp \tag{14}$$

in which Z is the compressibility factor that can be obtained from the equation of state [41,42]. Using eqs (2), (3) and (14), fugacity coefficient can be written as the expansion by pressure in which expansion coefficients depend on virial coefficients as follows:

$$\ln \varphi = \sum_{n=1} C_n P^n$$

$$C_1 = \frac{B}{RT} P$$

$$C_2 = \frac{1}{2R^2 T^2} \left(C - B^2 \right). \tag{15}$$

Figure 2. The calculated $A_0 = -(\partial H / \partial P)_T^0$ of SF_6 vs. temperature. (–) This work (from Zarkova equation), (···) this work (from Meng equation) and (○) experimental data.

It is clear that fugacity coefficient is equal to 1 when $P = 0$ and of course, at low pressure, second terms onwards can be ignored in the expansion.

3.4 *Thermal expansion*

In the general case of a gas, liquid, or solid, the volumetric coefficient of thermal expansion is given by

$$\alpha = \frac{1}{V_m} \left(\frac{\partial V_m}{\partial T} \right)_p. \tag{16}$$

It can be shown that thermal expansion depends on virial coefficient. At low pressure we have

$$\alpha = \frac{1}{V_m} \left(\frac{R}{P} + \frac{dB}{dT} \right). \tag{17}$$

4. Results and discussion

In this paper, we calculate some thermophysical properties of SF_6 using correlation equation. The model presented here for the prediction of thermodynamic properties of SF_6 covers the temperatures range $170 < T(K) < 1000$. The experimental data for thermophysical properties studied in this work are obtained from NIST [43] and these data for SF_6 are only between temperatures 230 and 520 K. Therefore, the comparison between the results of this work and the experimental data will be in that range of temperature.

The Boyle temperature (T_B) and Boyle volume (V_B) are found to be sensitive to the equation in use [44]. Therefore, we determined them using the correlation equation. The Boyle temperature (T_B) is the temperature in which $B(T_B) = 0$. The Boyle volume (V_B) can be
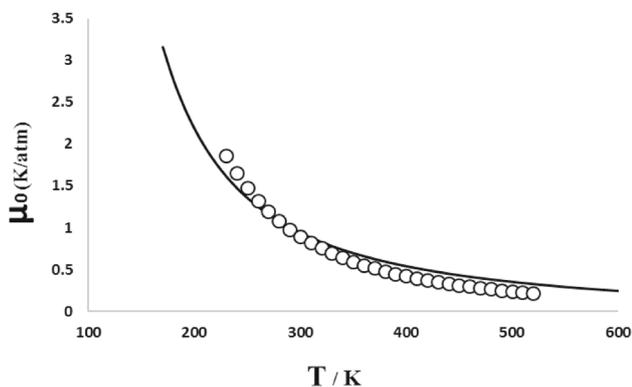
Figure 3. The calculated zero pressure J–T coefficient of SF_6 vs. temperature. (–) This work and (○) experimental data.
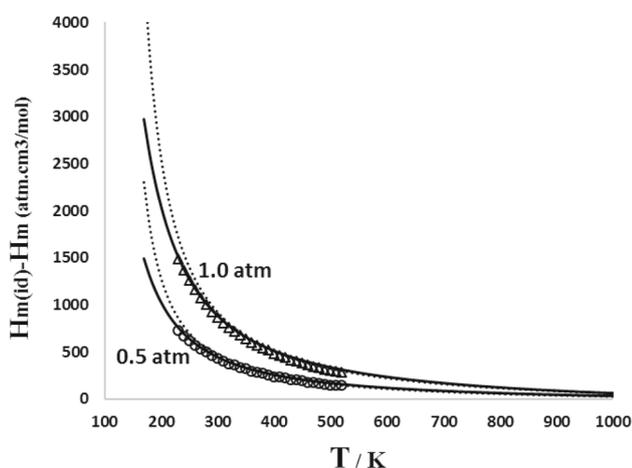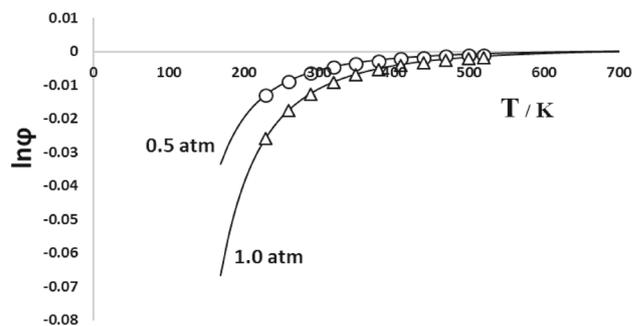

Figure 4. Deviation function of enthalpy for SF_6 for 0.5 atm and 1.0 atm pressures. (–) This work (from Zarkova equation), (···) this work (from Meng equation), (○) and (△) experimental data.

Figure 5. Variations of fugacity coefficient of SF_6 as a function of temperature for 0.5 atm and 1.0 atm pressures. (–) This work, (○) and (△) experimental data.

Figure 6. Variations of thermal expansion of SF_6 as a function of temperature. (–) This work (from Zarkova equation), (···) this work (from Meng equation) and (○) experimental data.
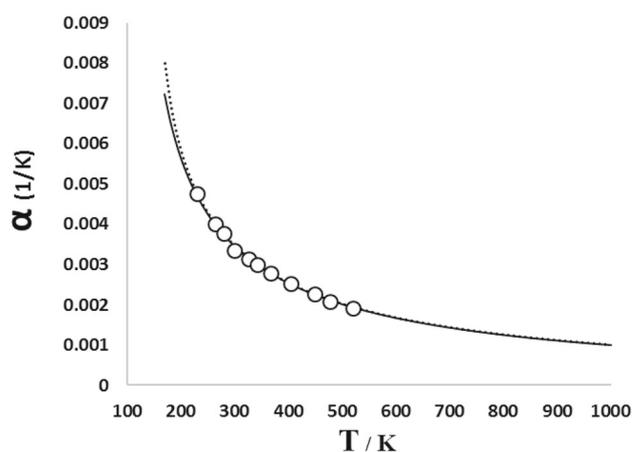
obtained as follows:

$$V_B = T_B \left(\frac{\partial B}{\partial T} \right)_{T=T_B}. \tag{14}$$

Based on the correlation equation for SF_6, $T_B = 677.2$ K and $V_B = 177.65$ cm^3/mol.

Figure 2 shows enthalpy changes with respect to pressure $A_0(= -(\partial H/\partial P)^0_T)$ of SF_6 as a function of temperature based on the two correlations of Zarkova and Meng. The results have been compared with the experimental data from NIST [43]. As can be seen, with decreasing temperature, especially temperatures below the critical temperature, $-(\partial H/\partial P)^0_T$ increases sharply, and with increasing temperature, this coefficient goes to zero. This behaviour of the fluid is predicted very well by the two correlation functions qualitatively and quantitatively. However, below 300 K, it seems that Zarkova equation presents better results than the experimental data.

Figure 3 shows the calculated zero pressure J–T coefficient of SF_6 vs. temperature using the corresponding state principle based on Zarkova equation. The obtained results are compared with the experimental data from NIST [43]. As can be seen, with decreasing temperature, especially temperatures below the critical temperature, μ^0_π increases sharply, and with increasing temperature, this coefficient goes to zero. This fluid behaviour is, both qualitatively and quantitatively, predicted well by the correlated equation in a wide range of temperature. Of course as observed, there is a deviation quantitatively between the calculated and experimental data. This is due to the approximation we have taken in deriving eq. (10). This approximation is explained in the previous paper [11].

Figure 4 shows the calculated deviation function of enthalpy for SF_6 vs. temperature for 0.5 and 1.0 atm pressures based on the two correlations of Zarkova and Meng. The results are compared with the experimental data from NIST [43]. As can be seen, there is a very good

Table 1. Temperature range and AAD% in thermophysical properties for SF_6.

Properties	Temperature range (K)	AAD%
μ_π^0	230–520	22.79
$A_0(T) = -\left(\frac{\partial H}{\partial P}\right)_T^0$	230–520	4.49
$H_m^{id}(T, P) - H_m(T, P)$ ($P = 0.5$ atm)	230–520	4.07
$H_m^{id}(T, P) - H_m(T, P)$ ($P = 1.0$ atm)	230–520	3.97
$\ln \varphi$ ($P = 0.5$ atm)	230–520	12.72
$\ln \varphi$ ($P = 1.0$ atm)	230–520	9.83
α	230–520	1.05

match between the experimental and theoretical results. However, as before, below 300 K, it seems that Zarkova equation presents better results than the experimental data.

Variations of fugacity coefficient of SF_6 as a function of temperature for 0.5 and 1.0 atm pressures are shown in figure 5 and the results are compared with the experimental data from NIST [43]. It is clear that, $\ln \varphi$ goes to zero with increasing temperature and decreases by increasing the pressure because of the increase in intermolecular forces. Correlation equation predicts very well this behaviour qualitatively and quantitatively.

Figure 6 shows the behaviour of thermal expansion of SF_6 vs. temperature based on two correlations of Zarkova and Meng compared with experimental data from NIST [43]. As observed, this behaviour is very well predicted by VEOS, and this indicates that the mentioned correlations are very good in determining the thermophysical properties of materials through virial coefficients.

For better consideration, table 1 shows average absolute deviation (AAD)% of the thermophysical properties of SF_6 calculated by this approach. As mentioned earlier, the comparison between the results of this work and the experimental data will be in the range of temperature $230 < T(\text{K}) < 520$. This range is also listed in table 1. It has been calculated using the following equation:

$$\text{AAD\%} = \frac{1}{\text{NP}} \sum \left| \frac{F_{\text{exp}} - F_{\text{calc}}}{F_{\text{exp}}} \right| \times 100 \qquad (15)$$

in which NP is the number of data points and F is the property studied.

5. Conclusion

In this paper, we calculated and modelled some thermodynamic functions at low pressure for SF_6 fluid to evaluate the performance of its correlation equation at low pressure and wide range of temperature. A review of the figures, tables and results shows that

1. Zarkova's correlation equation has a good ability to predict and model the thermophysical properties of SF_6 and its deviation from the ideal state.
2. If the virial coefficients are determined accurately, the thermodynamic properties of fluids can be calculated and predicted with good accuracy.
3. As virial coefficients are a connection bridge between the microscopic and macroscopic properties of the materials, thermodynamic and non-ideal behaviour of real fluids can be explained very well in this approach.
4. This study shows that the use of accurate virial coefficients and virial equation of state (VEOS) is suitable for modelling and predicting many thermophysical properties of the fluids.

Of course, other thermodynamic functions like bulk modulus, entropy deviation function, determination of intermolecular potentials via inversion method and so on can be calculated using virial coefficients. These studies will be our future work.

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