

## Determination of thermodynamic properties of some engineering fluids using two-constant equations of state

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### Abstract

Analytical formulae, rather than tables of thermodynamic and physical properties of important engineering materials over different ranges of operating conditions, are desired for performance analysis of many industrial and research applications.

Many equations of state, using different number of variables, have been suggested but the simplest are the two-constant equations of state, such as the Soave–Redlich–Kwong (SRK) and the Peng–Robinson (PR) equations. The two equations are used, in this work, to predict thermodynamic properties such as pressure, internal energy, enthalpy, and entropy for steam, R12 and ammonia in the superheated region, in addition to  $\text{NH}_3\text{--H}_2\text{O}$  solution.

Results of detailed calculations using a specially devised computer program showed that the SRK and PR equations give relatively low errors over wide regions. This justifies their utility over empirical multiconstant complex equations, for engineering computations. © 1997 Published by Elsevier Science B.V.

### 1. Introduction

Since the pioneering work of van der Waals (VDW) in 1873 [1], new equations of state have been developed in order to meet the over-stringent demand of the users of these equations for a more precise representation of data for fluid systems of industrial importance. The most important equation proposed as a modification for the VDW was that by Redlich and Kwong [2]. Many other researchers [3–6] have developed more accurate equations, starting from the RK equation. Other researchers have often tended towards greater complexity, especially the empirical type of formulation [7].

Although these more complex equations have their place, for example, in generating tables of accurate

thermodynamic data, a need still exists for a relatively simple formulation containing no more than two derived constants. These cubic two-constant equations represent a compromise between the more precise but computationally harder-to-use multiconstant equations, and the very simple though less accurate equations, having a wide range of applications, were those due to Soave–Redlich–Kwong [8] and the Peng–Robinson [9–11]. Therefore, these equations of state are used in this work in view of their expected accuracy in predicting pressure, internal energy, enthalpy, and the entropy for industrially important substances such as steam, Freon-12,  $\text{NH}_3\text{--H}_2\text{O}$  mixture and ammonia over different ranges of operating conditions in the superheated range, below the critical point as well as above saturated vapour region.

The predicted data from the PR and SRK equations are plotted against temperature to show their variation

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from the tabulated data predicted by the multiconstant equations. Detailed calculations of thermodynamic properties were performed using a specially devised computer program. The variation of pressure in comparison with tabulated values for steam, R12, and NH<sub>3</sub> is shown in the graphical form.

The variation of error in each property with temperature and pressure for each substance is shown in relevant figures. Results of error analysis for the NH<sub>3</sub>–H<sub>2</sub>O mixture, in comparison with the chart for different concentrations, are also shown.

## 2. Mathematical analysis

Many equations were proposed for estimating thermodynamic properties of gases, some of these being the ideal equation and the van der Waals equation. Van der Waals introduced two constants in the ideal gas equation to account for the volume occupied by gas molecules and the intermolecular forces [1]. Following that, several modifications were made in the VDW equation to improve its potential predictability, especially near the critical region where most of the generalized equations start to fail. These modifications were made by Redlich and Kwong [2], Wilson [3], Soave [4] and Barnes [5]. To improve predictability, further modifications were made by Soave–Redlich–Kwong [8] and Peng–Robinson [9]. The last two modifications are considered to be the most accurate, so far, for the two-constant generalized equations [12]. Therefore, they will be discussed here in detail.

### 2.1. Soave–Redlich–Kwong equation

The general form of the equation is given in Ref. [6] as follows:

$$Z \equiv \frac{PV}{RT} = \frac{V}{V-b} - \frac{\Omega_a b}{\Omega_b(V+b)} F \quad (1)$$

where  $\Omega_a = 0.42747$ ,  $\Omega_b = 0.08664$  and  $b = \Omega_b RT_c / P_c$  and

$$F = \frac{1}{T_r} [1 + (0.48 + 1.574\omega + 0.176\omega^2) \times (1 - \sqrt{T_r})]^2 \quad (2)$$

$$\omega = -\log_{10}(P_{r,S})|_{T_r=0.7} - 1$$

### 2.1.1. Derivation of thermodynamic properties

Let  $\Omega_a/\Omega_b = y$ ,  $0.48 + 1.574\omega + 0.176\omega^2 = k$ , and  $T_r = T/T_c$ , then Eq. (1) will be:

$$Z \equiv \frac{PV}{RT} = \frac{V}{V-b} - y \frac{b}{V+b} \frac{T_c}{T} \times \left[ 1 + k \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \quad (3)$$

from Eq. (3)

$$P \equiv \frac{ZRT}{V} = \frac{RT}{V} \left\{ \frac{V}{V-b} - y \frac{b}{V+b} \frac{T_c}{T} \times \left[ 1 + k \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \right\}$$

or

$$P = \frac{RT}{V-b} - \frac{RbyT_c}{V(V+b)} \left[ 1 + k \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \quad (4)$$

Eq. (4) can be used to calculate the pressure of any substance.

Changes in internal energy can be shown to be as follows:

$$dU = C_v dt + \left[ T \left( \frac{\partial P}{\partial T} \right)_v - P \right] dV,$$

hence

$$(U_2 - U_1) = \int_{T_1}^{T_2} C_v dT + \int_{V_2}^{V_1} \left[ T \left( \frac{\partial P}{\partial T} \right)_v - P \right] dV \quad (5)$$

Along an isotherm, the foregoing equation will become

$$(U_2 - U_1)_T = \int_{V_1}^{V_2} [T(\partial P/\partial T)_v - P] dV \quad (6)$$

After some manipulations and rearrangements, Eq. (6) becomes

$$\begin{aligned}
 (U_2 - U_1)_T & \\
 & \equiv \int_{V_1}^{V_2} \left\{ \frac{RbyT_c}{V(V+b)} \left[ 1+k \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right] (1+k) \right\} dV \\
 & = RbyT_c \left[ 1+k \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right] (1+k) \\
 & \quad \times \int_{V_1}^{V_2} \frac{1}{V(V+b)} dV \quad (7)
 \end{aligned}$$

Hence

$$\begin{aligned}
 (U_2 - U_1)_T & = RbyT_c \left[ 1+k \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right] \\
 & \quad \times (1+k) \frac{1}{b} \ln \left| \frac{V_2(V_1+b)}{V_1(V_2+b)} \right|
 \end{aligned}$$

and Eq. (5) will be

$$\begin{aligned}
 (U_2 - U_1) & = \int_{T_1}^{T_2} C_v dT + RyT_c \left[ 1+k \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right] \\
 & \quad \times (1+k) \ln \left| \frac{V_2(V_1+b)}{V_1(V_2+b)} \right| \quad (8)
 \end{aligned}$$

where the  $C_v$  equations for substances used in this work are given in Ref. [13]. The change in enthalpy is calculated from the following equation:

$$H_2 - H_1 = u_2 - u_1 + P_2 V_2 - P_1 V_1 \quad (9)$$

To calculate the entropy, it can be shown that

$$dS = C_v \frac{dT}{T} + \left( \frac{\partial P}{\partial T} \right)_v dV$$

or

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{C_v}{T} dT + \int_{V_1}^{V_2} \left( \frac{\partial P}{\partial T} \right)_v dV \quad (10)$$

After some manipulations and rearrangements, Eq. (10) becomes

$$\begin{aligned}
 S_2 - S_1 & = \int_{T_1}^{T_2} \frac{C_v}{T} dT + R \ln \left| \frac{V_2 - b}{V_1 - b} \right| \\
 & \quad + Ryk \sqrt{\frac{T_c}{T}} \left[ 1+k \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right] \\
 & \quad \times \ln \left| \frac{V_2(V_1+b)}{V_1(V_2+b)} \right| \quad (11)
 \end{aligned}$$

## 2.2. Peng–Robinson equation

The general form of the equation is

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b(V-b)} \quad (12)$$

where:

$$a(T) = a(T_c) \alpha(T_r, \omega)$$

$$a(T_c) = 0.45724R^2 T_c^2 / P_c$$

$$\alpha(T_r, \omega) = [1 + k(1 - \sqrt{T_r})]^2$$

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

$$b = 0.778RT_c / P_c$$

$$T_r = T/T_c$$

### 2.2.1. Derivation of thermodynamic properties

The general form of the equation can be written as follows:

$$P = \frac{RT}{v-b} - \frac{a(T_c) \left[ 1+k \left( 1 - \sqrt{T/T_c} \right) \right]^2}{v(v+b) + b(v-b)} \quad (13)$$

Following a procedure similar to that used with the SRK equation, the changes in internal energy can be derived. Hence

$$\begin{aligned}
 (U_2 - U_1)_T & \\
 & = a(T_c) \left[ 1+k \left( 1 - \sqrt{T/T_c} \right) \right] (1+k) \frac{1}{2\sqrt{2b}} \\
 & \quad \times \ln \frac{(v_2 + b - \sqrt{2b})(v_1 + b + \sqrt{2b})}{(v_1 + b + \sqrt{2b})(v_2 + b - \sqrt{2b})}
 \end{aligned}$$

and

$$\begin{aligned}
 (U_2 - U_1)_T & \\
 & = \int_{T_1}^{T_2} C_v dT + a(T_c) \left[ 1+k \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right] (1+k) \\
 & \quad \times \frac{1}{2\sqrt{2b}} \ln \left| \frac{(v_2 + b - \sqrt{2b})(v_1 + b + \sqrt{2b})}{(v_2 + b + \sqrt{2b})(v_1 + b - \sqrt{2b})} \right| \quad (14)
 \end{aligned}$$

The change in enthalpy can be calculated from Eq. (9). After some manipulations of Eq. (10),

entropy change is given by

$$dS = \int_{T_1}^{T_2} \frac{C_V}{T} dT + \int_{V_1}^{V_2} \frac{R}{V-b} dV + a(T_c)$$

$$\times \left[ 1 + k \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right] \frac{k}{\sqrt{T-T_c}} \int_{V_1}^{V_2}$$

$$\times \frac{1}{V(V+b) + b(V-b)} dV$$

This equation is integrated to yield

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{C_V}{T} dT + R \ln \left| \frac{V_2 - b}{V_1 - b} \right| + a(T_c)$$

$$\times \left[ 1 + k \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right] \frac{k}{\sqrt{T_c} 2\sqrt{2b}}$$

$$\times \ln \left| \frac{(V_2 + b - \sqrt{2b})(V_1 + b + \sqrt{2b})}{(V_1 + b + \sqrt{2b})(V_1 + b - \sqrt{2b})} \right|$$

### 3. Discussion of results

As shown here, relations have been developed, using SRK and PR equations of state, to calculate  $U$ ,  $H$ , and  $S$ . The reference point was taken as the saturated vapour point at 273.16 K for steam, and 233.15 K for R12 and  $\text{NH}_3$ . Thus, prediction is related to the superheat region. Pressure was predicted from a knowledge of temperature and specific volume, without the need of referring to a specific reference point.

Figs. 1-6 show a comparison of predicted pressure using PR and SRK equations with experimental tabulated values for steam,  $\text{NH}_3$ , and R12, along constant pressure processes in the superheat region. It is noticed that disparity between prediction and experiment is negligible. Even in the critical region, the error does not exceed 3% in the PR and 9% in the SRK equations of state.

Figs. 7-12 show the predicted percentage error in the internal energy using PR and SRK equations for steam,  $\text{NH}_3$ , and R12, respectively, at different pressures and temperatures. This error is related to the second term on the right-hand side of Eq. (5), which is called here the internal energy deviation due to

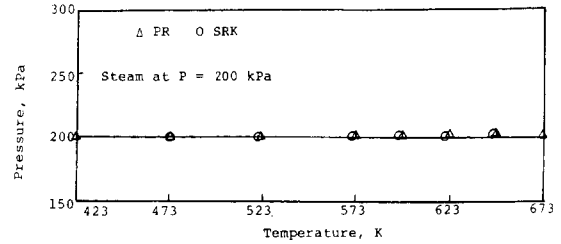


Fig. 1. Variation in pressure with temperature for steam using PR and SRK equations of state.

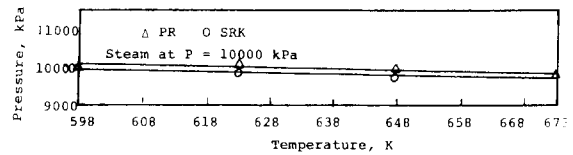


Fig. 2. Variation in pressure with temperature for steam using PR and SRK equations of state.

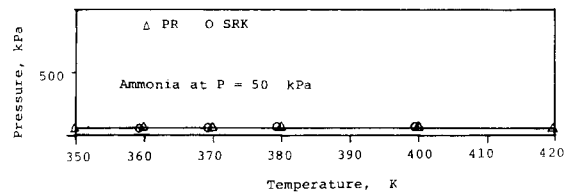


Fig. 3. Variation in pressure with temperature for ammonia using PR and SRK equations of state.

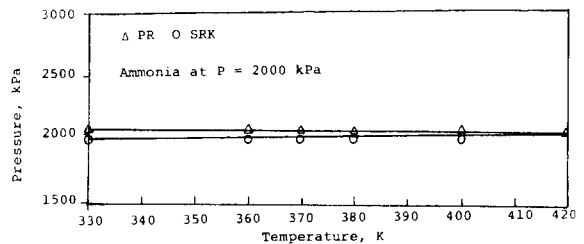


Fig. 4. Variation in pressure with temperature for ammonia using PR and SRK equations of state.

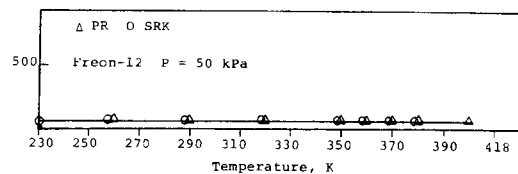


Fig. 5. Variation in pressure with temperature for Freon-12 using PR and SRK equations of state.

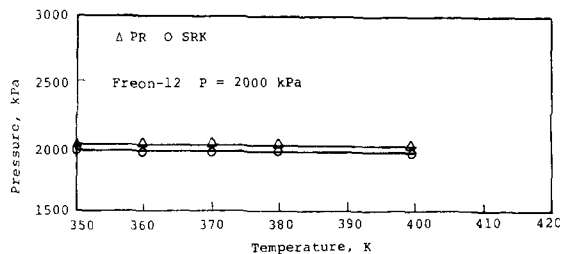


Fig. 6. Variation in pressure with temperature for Freon-12 using PR and SRK equations of state.

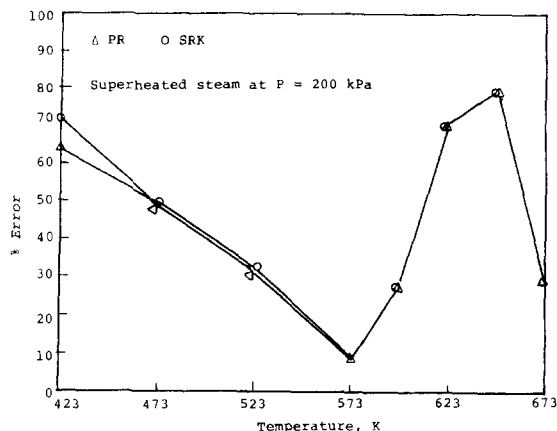


Fig. 7. Variation in error of internal energy deviation with temperature for steam using PR and SRK equations of state.

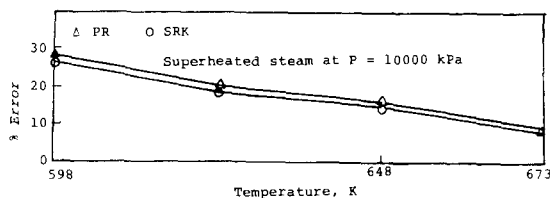


Fig. 8. Variation in error of internal energy deviation with temperature for steam using PR and SRK equations of state.

inclusion of 'V' as independent variable for the variation of U.

This percentage error in internal energy deviation at low and high pressures has maximum values at low pressures, especially at temperatures near the saturated vapour line. It amounts to 63.8 and 72.2% in the deviation term of PR and SRK equations at 200 kPa and 423 K as shown in Fig. 7. Fortunately, this high error in the deviation term is not significant in absolute terms, mainly because the deviation term contributes

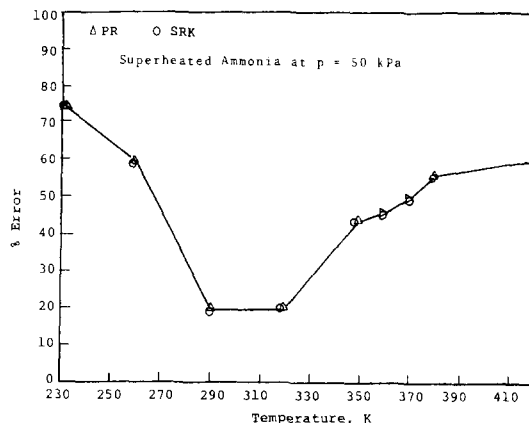


Fig. 9. Variation of error in internal energy deviation with temperature for ammonia using PR and SRK equations of state.

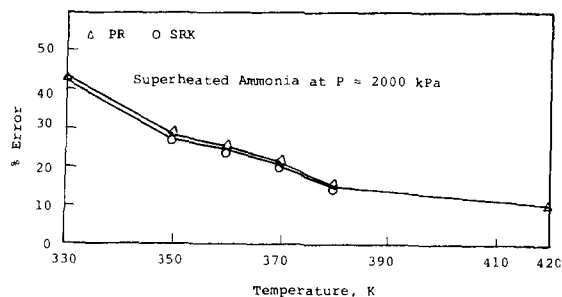


Fig. 10. Variation of error in internal energy deviation with temperature for ammonia using PR and SRK equations of state.

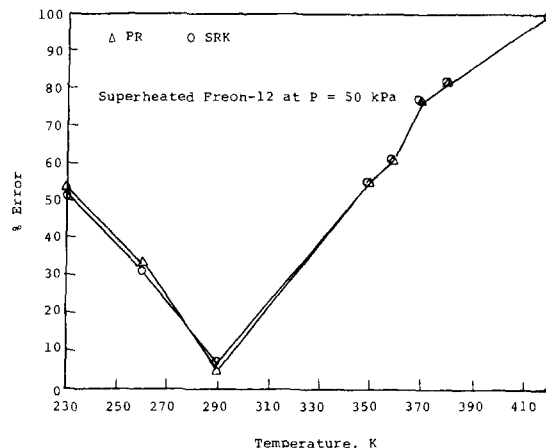


Fig. 11. Variation of error in internal energy deviation with temperature for Freon-12 using PR and SRK equations of state.

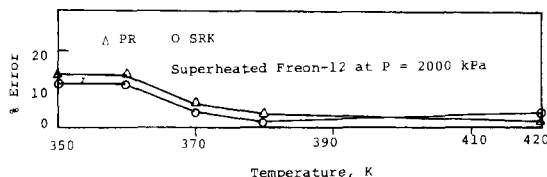


Fig. 12. Variation of error in internal energy deviation with temperature for Freon-12 using PR and SRK equations of state.

only  $\sim 6\%$  of the total internal energy (hence, 4% total). At higher temperatures, the error drops steeply, but rises again at specific temperatures for each substance and may be cyclic in the high temperature regions. At higher pressures, the level of error drops drastically, as shown in Fig. 8; where the pressure is 10 000 kPa at 673 K, the error is 9% in PR and 8% in SRK. The absolute error in internal energy is also low, as the deviation term contributes  $\sim 30\%$  of the total value (2.7% total). This has special significance in modern steam-powered stations. The above-mentioned trade-offs apply to  $\text{NH}_3$  and R12, with some variation in the corresponding values of error.

The figures showing the % error in entropy using PR and SRK equations for steam,  $\text{NH}_3$ , and R12 have been omitted to reduce the size of the paper. However, it is found that the error level is much lower than that predicted in internal energy deviation for all points with a maximum value less than 3% for different substances and conditions. The behaviour of entropy is interesting, especially because the deviation on account of entropy may contribute as high as 70% of the total entropy (i.e. 2.1% total deviation). Thus, an error in absolute entropy in the superheat region may

Table 1

Results of error analysis in predicting pressure for  $\text{NH}_3\text{-H}_2\text{O}$  solutions using PR and SRK equations of state

Solution/ $\text{NH}_3\%$	Pressure/ kPa	%Error PR	%Error SRK
50	2240	-2.61	8.25
	620	2.29	6.47
	207	1.76	3.33
70	2240	3.55	-2.49
	1103	2.8	-2.68
	310	1.53	-0.83
80	2240	8.47	-2.91
	1171.5	5.50	-1.19
	483	3.6	-0.054

easily be neglected when using SRK and PR equations.

The  $\text{NH}_3\text{-H}_2\text{O}$  solution was also investigated, due to its importance in the absorption cooling applications [14] and in some power and co-generation energy systems [15]. Table 1 shows the percentage error involved in predicting pressure using the SRK and PR equations for the ammonia solution with concentrations of 50, 70, and 80% of  $\text{NH}_3$ . The PR equation is more accurate for the 50% solution, whereas the SRK equation takes over with higher concentrations. Table 2 shows the percentage error involved in predicting the enthalpy using the same equations, solution concentrations and pressures. It is interesting to note that the PR is more accurate for the investigated range of operating conditions.

Table 2

Results of error analysis in predicting enthalpy for  $\text{NH}_3\text{-H}_2\text{O}$  solutions using PR and SRK equations of state

Solution/ $\text{NH}_3\%$	Pressure/kPa	Temperature/ $^{\circ}\text{C}$	Enthalpy/kJ/kg	% Error (PR)	% Error (SRK)
50	2240	97	1453	-0.56	9.98
	620	42	1372	-0.89	10.29
	207	13	1326	-1.13	10.65
70	2240	72	1393	3.11	5.64
	1103	40	1344	1.005	5.72
	310	4.4	1287	0.58	6.59
80	2240	66	1372	2.51	8.22
	1171.5	40	1335	0.77	6.72
	483	10	1287	0.55	4.88

#### 4. Conclusions

1. Analysis of results using PR and SRK equations shows that maximum predicted errors exist near the critical point and in the region adjacent to the saturated vapour line especially at low pressure and temperature. It was 4% in total internal energy, and 2.1% in total entropy.
2. The relatively low errors involved in the superheat region of many fluids as steam, R12 and NH<sub>3</sub> when using generalized two-constant equations such as PR and SRK, render their use a great advantage over empirical multiconstant complex equations.
3. The PR equation gives better accuracy when used to calculate  $P$ ,  $U$ , and  $H$  for steam and NH<sub>3</sub>, whereas SRK equation is relatively superior with R12 and entropy calculations for the three substances.
4. The analysis of the NH<sub>3</sub>-H<sub>2</sub>O solution shows that the PR equation outperforms the SRK one in predicting enthalpy over the range of operating conditions. With regard to pressure, it is predicted more accurately by the SRK equation except for the 50% solution.

#### 5. Nomenclature

$a$	coefficient in the PR equation
$b$	coefficient in the PR equation
$C_V$	specific heat at constant volume, kJ/kg K
$C_P$	specific heat at constant pressure, kJ/kg K
$H$	enthalpy, kJ/kg
$P$	pressure, kPa
$P_c$	critical pressure, kPa
$P_r$	reduced pressure
PR	Peng–Robbinson equation of state
$R$	universal gas constant, kJ/mol K
$S$	entropy, kJ/kg K
SRK	Soave–Redlich–Kwong equation of state
$T$	temperature, K

$T_c$	critical temperature, K
$T_r$	reduced temperature
$U$	internal energy, kJ/kg
$V$	specific volume on molal basis, m <sup>3</sup> /k mol
$Z$	compressibility factor
$\omega$	acentric factor

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