

## **New Equation for Vapor Pressures of Difluoromethane (HFC-32)<sup>1</sup>**

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Critically evaluated experimental vapor-pressure data sets supplemented with calculated data for low-temperature region were used in the development of vapor-pressure equations. The optimum number of terms, coefficients, and exponents of the Wagner-type equation were derived by means of the Setzmann-Wagner program OPTIM based on the combination of the stepwise regression analysis and evolutionary optimization method. Equations were checked by the reduced enthalpy of vaporization criterion derived from the Clausius-Clapeyron equation and specific volume of ideal gas. An equation developed using 261 experimental data points and low-temperature data calculated by Lüddecke and Magee gives an RMS deviation of 0.102%; a second equation based on the same experimental data and low-temperature data calculated by Tillner-Roth gives an RMS deviation of 0.101% from experimental points. The triple-point pressure extrapolated to the measured temperature  $T_{tp} = 136.34$  K is discussed. Comparisons with vapor pressure equations by Outcalt and McLinden, Duarte-Garza and Magee, and Kubota et al. are also given.

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**KEY WORDS:** critical point; difluoromethane; HFC-32; triple point; vapor pressure equation.

### **1. INTRODUCTION**

The vapor pressure of difluoromethane (HFC-32) was intensively measured in the temperature range from 149 K to the critical point [1]. More

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then 20 vapor-pressure equations for HFC-32 which usually describe the measured range only or correlate a limited number of measured data sets can be found in the literature. Most methods for measurements in the low-pressure region (below approx. 150 kPa) are time-consuming and relatively inaccurate [2]. Recently estimation procedures appeared in the literature which can be used to extrapolate high-accuracy vapor pressure data down to the triple point [3–5]. The aims of our work are the critical evaluation of measured vapor-pressure data, and with the aid of derived low-pressure data by estimation procedures, a representation of vapor pressures over the entire temperature range from the triple to the critical point using a Wagner-type equation.

## 2. CRITICAL EVALUATION OF MEASURED VAPOR PRESSURE DATA

From all experimental vapor-pressure data sets [6–25] 14 data sets [7, 13–25] were included in the evaluation process. The two most reliable vapor-pressure equations were selected from more than 20 equations, and the deviations of particular data and data sets were calculated. Both equations were of the Wagner type,

$$\ln(p/p_c) = (T_c/T) \sum a_i \tau^i, \quad \tau = 1 - (T/T_c) \quad (1)$$

which provides an accurate description of the vapor pressure over the entire temperature range. The first equation with three constants was derived by Kubota et al. [6] for the range between 208 K and  $T_c$ ; it can be used to correlate reported data [7, 11–13, 15] within  $\pm 5$  mK. The second equation with five constants was derived by Outcalt and McLinden [29] using data of Defibaugh [21], Holcomb [14], and those derived from the saturated heat capacity by Lüddecke and Magee [3]. The RMS deviation between data used for correlation and calculated values is 0.023%.

For the selected measured points, the absolute deviation ( $\Delta p$ ) and percentage deviation ( $\delta p$ ) are calculated as follows:

$$\Delta p = p_{\text{exp}} - p_{\text{eq}}, \quad \delta p = 100 \Delta p / p_{\text{exp}} \% \quad (2)$$

For the selected data sets, the following statistical relations are defined.

Absolute average deviation:

$$AAD = \frac{1}{n} \sum |\delta p_i| \% \quad (3)$$

**Table I.** Statistical Deviations of Selected Experimental Data from the Kubota et al. [6] and Outcalt and McLinden [29] Equations

Ref.	Eq.	AAD (%)	SDV (%)	BIAS (%)	RMS (%)	No. of points
[7]	Kub.	0.2327	0.2877	0.0148	0.2829	(30) (29) <sup>a</sup>
	O. + McL.	0.2309	0.2795	0.0421	0.2778	
[13]	Kub.	0.0360	0.0447	-0.0204	0.0468	9
	O. + McL.	0.0360	0.0423	-0.0098	0.0411	
[14]	Kub.	0.1165	0.1750	0.0582	0.1811	25
	O. + McL.	0.1156	0.1554	0.0880	0.1759	
[15]	Kub.	0.0397	0.0432	0.0231	0.0483	27
	O. + McL.	0.0259	0.0337	0.0006	0.0330	
[16]	Kub.	0.2469	0.2942	0.0287	0.2910	32
	O. + McL.	0.2439	0.2855	0.0410	0.2869	
[17]	Kub.	0.0550	0.0602	0.0441	0.0737	(30) 27
	O. + McL.	0.0552	0.0515	0.0542	0.0741	
[18]	Kub.	0.0601	0.0800	0.0075	0.0796	58
	O. + McL.	0.0660	0.0847	0.0259	0.0878	
[19]	Kub.	0.0317	0.0455	-0.0003	0.0442	17
	O. + McL.	0.0184	0.0474	0.0120	0.0475	
[20]	Kub.	0.3855	0.5054	-0.2622	0.5603	25
	O. + McL.	0.3741	0.5093	-0.2579	0.5617	
[21]	Kub.	0.0279	0.0286	-0.0171	0.0326	18
	O. + McL.	0.0065	0.0092	-0.0013	0.0090	
[22]	Kub.	0.0235	0.0240	0.0169	0.0289	(21) 18
	O. + McL.	0.0349	0.0170	0.0348	0.0386	
[23]	Kub.	0.1831	0.2001	0.1338	0.2301	8
	O. + McL.	0.1937	0.2084	0.1486	0.2451	
[24]	Kub.	0.1033	0.0415	-0.1033	0.1102	7
	O. + McL.	0.0923	0.0361	-0.0923	0.0981	
[25]	Kub.	0.1010	0.1248	-0.0872	0.1543	57
	O. + McL.	0.0952	0.1304	-0.0680	0.1461	

<sup>a</sup> Points with  $T > T_c = 351.255$  K were omitted.

Systematic deviation:

$$BIAS = \frac{1}{n} \sum \delta p_i \% \quad (4)$$

Standard deviation:

$$SDV = \sqrt{\frac{\sum (\delta p_i - BIAS)^2}{n - 1}} \% \quad (5)$$

Root-mean square deviation:

$$RMS = \sqrt{\frac{1}{n} \sum (\delta p_i)^2} \% \quad (6)$$

The survey of statistical deviations of selected data sets from Kubota et al., and from Outcalt and McLinden equations is given in Table I.

Measurements from Refs. 13–15, 17–22, 24, and 25 were selected as reliable for further analysis.

### 3. ESTIMATED VAPOR PRESSURE DATA AT LOW PRESSURES

Lüddecke and Magee [3] derived vapor-pressure data at pressures lower than 6.798 kPa from the saturated liquid heat capacity measurements by applying a thermodynamic relationship between the saturated liquid heat capacity and the temperature derivatives of the vapor pressure, by a method devised by Baehr [27].

Tillner-Roth's method [4] involves a nonlinear regression analysis based on the Clausius–Clapeyron equation and a simple relation of the enthalpy of vaporization. He estimated 49 low-pressure data ranging from  $T_{tp}$  to 232 K.

The method of Duarte-Garza and Magee [5] starts from the measured internal-energy changes (data calculated from an equation of state or, alternatively, experimental caloric data may be employed) and reference value of the vapor pressure and its derivative with respect to temperature evaluated near the normal boiling point temperature.

### 4. DEVELOPMENT OF THE VAPOR PRESSURE EQUATION

The Wagner–Setzmann program OPTIM [26], based on the stepwise regression analysis connected with the evolutionary optimization method, was employed for the search to determine the optimum number of terms, appropriate coefficients, and exponents of the Wagner-type vapor pressure equation with critical parameters  $T_c = 351.26$  K and  $p_c = 5.785$  MPa. The investigation started with the maximum number of terms equal to 6, and the step for exponents  $n_i$  was chosen as 1/2, but other steps of 1/4 and 1/3 were tested.

In parallel with the regression analysis, the behavior of the reduced enthalpies of vaporization derived from the Clausius–Clapeyron equation and ideal gas equation of state was evaluated in the low-temperature region up to 180 K. If the difference between the specific volume of the saturated

vapor and saturated liquid in the Clausius–Clapeyron equation is replaced by the specific volume of the ideal gas, the specific enthalpy of vaporization in dimensionless form is

$$\frac{\Delta h_{\text{id}}}{RT} = T \frac{d \ln(p_s)}{dT} \quad (7)$$

The derivative of vapor pressure was calculated from the tested equation. For calculations based on the data points of Lüddecke and Magee [3] and of Tillner-Roth [4], the previous equation was integrated. Over a short temperature range,  $\Delta h_{\text{id}}$  can be considered as a constant.

Then, for the two neighboring data points the relation

$$\frac{\Delta h_{\text{id}}}{RT_M} = \frac{T_M}{T_2 - T_1} \ln \left( \frac{p_{s2}}{p_{s1}} \right) \quad (8)$$

holds, where the mean temperature is  $T_M = \sqrt{T_1 T_2}$ .

Use of the ideal gas specific volume in the Clausius–Clapeyron equation has a small influence on the reduced enthalpy of vaporization in the neighborhood of the triple point. At 140 K the estimated deviation is less than 0.03%, and at 180 K, less than 0.6%.

## 5. RESULTS

The experimental data sets, Refs. 13–15, 17–19, 21, 22, 24, and 25, were finally used in the development of the vapor-pressure equation supplemented with two low-temperature data sets [3, 4]. There is considerable difference between these data sets [3, 4], namely, at low temperatures. The deviations are given in Table II.

**Table II.** Differences Between Vapor Pressures at Low Temperatures

$T$ (K)	$p_s$ [3] (Pa)	$p_s$ [4] (Pa)	$\Delta p_s$ (Pa)	$\delta p_s$ (%)
140	81.0	87.5	–6.5	–8.02
150	319.0	334.6	–15.6	–4.89
160	1026.0	1061.0	–35.0	–3.41
170	2818.0	2887.2	–69.2	–2.45
180	6798.0	6926.3	–128.3	–1.88

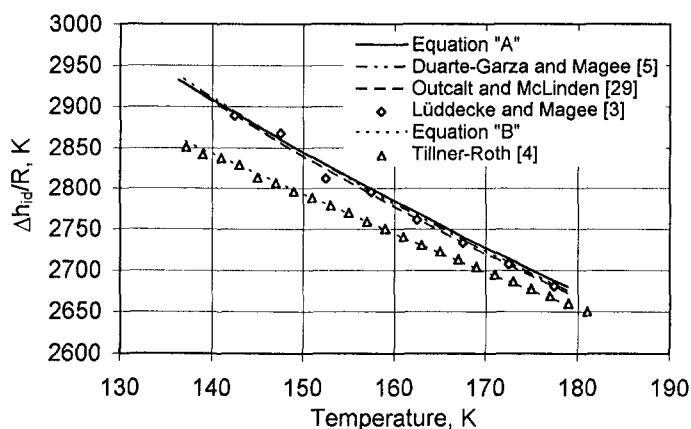


Fig. 1. Reduced enthalpy of vaporization; points are from calculated values, and lines from vapor pressure equations.

The values of the reduced enthalpies of vaporization from different sources exhibit significant differences as shown in Fig. 1. This was the main reason to carry out detailed independent analysis with data sets in Refs. 3 and 4.

A simple accurate auxiliary equation was developed for data from Ref. 3. Very good agreement for the reduced enthalpy of vaporization was attained. The extrapolation gave the triple point pressure  $p_{tp} = 46.3$  Pa at  $T_{tp} = 136.34$  K for data from Ref. 3.

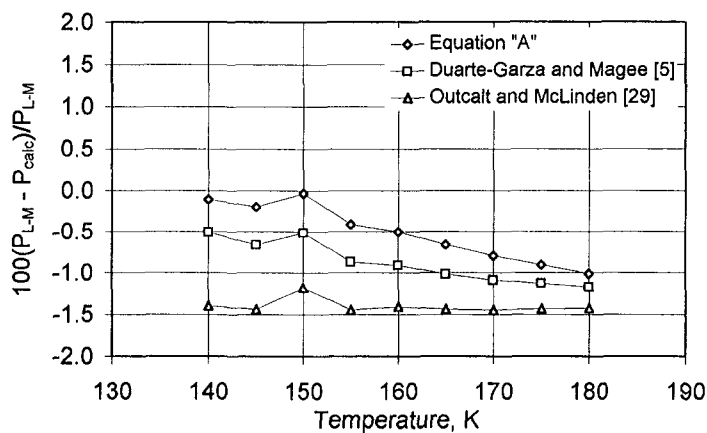


Fig. 2. Deviations of vapor pressures of Lüddecke and Magee [3] ( $P_{L-M}$ ) and calculated values ( $P_{calc}$ ) from different equations.

The vapor-pressure equation developed from the experimental data sets mentioned above and data from Ref. 3 is denoted as equation "A." Its parameters are given in Table III, together with equations by Outcalt and McLinden [29], Duarte-Garza and Magee [5], and Kubota et al. [6]. Statistical deviations for 10 selected data sets are included in Table III, as well as the local deviations of several data points by Lüddecke and Magee [3]. These deviations for all data points are shown in Fig. 2. Curves of the reduced enthalpy of vaporization  $\Delta h_{id}/R$  is presented in Fig. 1.

**Table III.** Parameters of Vapor Pressure Equation "A" and Those of Outcalt and McLinden [29], Duarte-Garza and Magee [5], and Kubota et al. [6]

	Eq. "A" (this work)	Outcalt/McLinden [29]	Duarte-Garza/ Magee [5]	Kubota et al. [6]
$a_1$	-7.53814480	-7.559554	-7.566935	-7.433405
$a_2$	2.35886776	2.465252	2.484133	1.522618
$a_3$	-1.88421329	-1.976887	-1.984020	-2.902286
$a_4$	-3.34123534	-2.021284	-2.067412	0
$a_5$	0	-1.941251	-1.921275	0
$n_1$	1	1	1	1
$n_2$	1.5	1.5	1.5	1.5
$n_3$	2	2	2	2
$n_4$	4.5	6	6	—
$n_5$	—	6.5	6.5	—
$T_c$ (K)	351.26	351.35	351.35	351.225
$p_c$ (MPa)	5.785	5.795	5.795	5.780
$T_{nbp}$ (K)	221.484	221.491	221.500	221.500
$p_{tp}$ (Pa)	46.3	46.9	46.5	—
Statistical deviations from experimental data				
AAD (%)	0.0629	0.0624	0.0709	0.0666
BIAS (%)	-0.00177	-0.00595	0.02816	-0.00775
SDV (%)	0.1018	0.1027	0.1045	0.1056
RMS (%)	0.1016	0.1027	0.1080	0.1057
Percentage deviations from data of Lüddecke and Magee [3]				
$T$ (K)	140	160	180	
	-0.106	-0.498	-1.011	
	-1.397	-1.404	-1.425	
	-0.506	-0.911	-1.170	
Band of percentage deviations from data of Refs. 15 and 19 up to 240 K				
From	-0.071	-0.082	-0.0	-0.06
To	0.070	0.055	0.135	0.09

Table IV. Parameters of Equation "B"<sup>a</sup>

$a_1 = -7.52623115$	$n_1 = 1$	AAD (%) = 0.0600
$a_2 = 2.25589183$	$n_2 = 1.5$	BIAS (%) = -0.00436
$a_3 = -1.66291028$	$n_3 = 2$	SDV (%) = 0.1009
$a_4 = -2.65474971$	$n_4 = 4$	RMS (%) = 0.1008

<sup>a</sup>  $T_c = 351.26$  K;  $p_c = 5.785$  MPa;  $T_{\text{nop}} = 221.488$  K;  $p_{\text{tp}} = 50.70$  Pa

Separate evaluation of the same experimental data sets [13–15, 17–19, 21, 22, 24, 25] together with the data of Tillner-Roth [4] led to the vapor-pressure equation indicated as "B." Its parameters are given in Table IV, including statistical deviations. Deviations from data points [4] are shown in Fig. 3, and the curves for the reduced enthalpy of vaporization  $\Delta h_{\text{id}}/R$  in Fig. 1. The maximum deviation from Tillner-Roth's data is  $-0.25\%$ .

## 6. CONCLUSION

Fourteen experimental data sets were analyzed, and 10 of them were used for the development of the new vapor-pressure equation. Two low-temperature data sets were analyzed separately. Because of a large discrepancy between the data of Lüddecke and Magee [3] and of Tillner-Roth [4], two different vapor pressure equations were developed. They are indicated as "A" and "B."

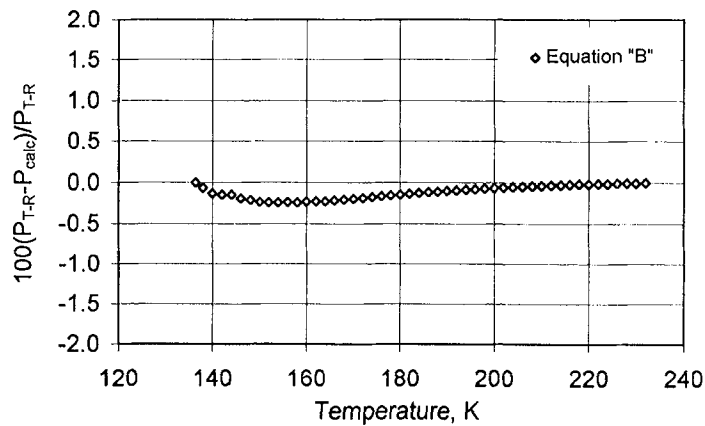


Fig. 3. Deviations of vapor pressures of Tillner-Roth [4] ( $P_{T-R}$ ) and calculated values ( $P_{\text{calc}}$ ) from equation "B."



Equation "A" has a lower number of terms and smaller deviations from experimental data sets than do equations by Outcalt and McLinden [29] and Duarte-Garza and Magee [5] (see Table III). It has much smaller deviations from the data of Lüddecke and Magee [3], especially close to the triple point. The value of the triple-point pressure calculated from equation "A" is 46.3 Pa, which differs little from the value of 46.5 Pa, calculated from the equation of Duarte-Garza and Magee [5]. The equation of Outcalt and McLinden gives 46.9 Pa.

It is remarkable that deviations of all equations mentioned above have the same sign from the data by Lüddecke and Magee. Judging by deviations of the Outcalt and McLinden equation, these data could be suspect based on the observed systematic deviations. But, the deviations of Duarte-Garza and Magee decrease when approaching the triple point, the same behavior as observed for equation "A" (Fig. 2).

Equation "B" also has very small deviations comparing to the experimental data sets and the calculated values of Tillner-Roth. The triple-point pressure reported by Tillner-Roth [4] is quite different from the value discussed above. It is 50.70 Pa, which is the same value as determined from equation "B". The precision of the values of Tillner-Roth [4] is dependent on the accuracy of the simple one-term equation of the enthalpy of vaporization which he used.

Both vapor-pressure equations "A" and "B" represent correlated data sets with practically the same statistical deviations (see Tables III and IV). The low-pressure data are questionable. All three estimation procedures [3–5] are correct from the thermodynamic point of view. However, the results are dependent on the input data used, what influences appreciably the triple-point pressure calculated for the measured temperature  $T_{tp}$ . In our opinion, the real value of the triple-point pressure probably lies between the predicted values of Lüddecke and Magee and Tillner-Roth. To verify this, a comprehensive analysis of the thermodynamic surface is needed.

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