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## ACCURATE VAPOR PRESSURES FOR REFRIGERANTS

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### ABSTRACT

Parameters for a new vapor pressure equation are reported for methane, ethane, propane, *n*-butane, *i*-butane, R-11, R-12, R-22, R-23, R-32, R-123, R-134a, R-141b, R-142b, R-143a and R-152a. These parameters have been obtained using experimental vapor pressures reported in the literature. The vapor pressure equation is based on asymptotic behavior at the triple and critical points, and it has three fluid dependent parameters. This equation describes the entire vapor pressure curve within the approximate accuracy of the experimental values.

### NOMENCLATURE

- $a_i$  = parameters for vapor pressure equation
- $b_i$  = parameters for vapor pressure equation
- $N$  = empirical constant of vapor pressure equation
- $p$  = reduced vapor pressure variable
- $p_0$  = asymptotic vapor pressure behavior approaching the triple point
- $p_\infty$  = asymptotic vapor pressure behavior approaching the critical point
- $\Delta p$  = difference between experimental and calculated values of  $p$
- $P^\sigma$  = vapor pressure
- $\delta P^\sigma$  = difference between experimental and calculated vapor pressures
- $P_c$  = critical pressure
- $P_t$  = triple point pressure
- $\sigma_i(P)$  = variance of pressure measurement
- $\sigma_i(T)$  = variance of temperature measurement
- $R$  = universal gas constant
- $SS$  = weighted sum of squares in statistical procedure
- $t$  = reduced temperature variable
- $T$  = temperature
- $T_c$  = critical temperature
- $T_t$  = triple point temperature
- $W_i$  = statistical weighting factor for datum  $i$

## INTRODUCTION

Accurate vapor pressures are important for the design of process equipment, especially in the field of refrigeration and air conditioning. Many vapor pressure equations have appeared in the literature, but, in general, the equations which describe experimental data within the accuracy of the measurements are quite complex if the entire vapor pressure curve (from the triple point to the critical point) is described with a single function. Alternatively, simple functions such as the Antoine equation can describe vapor pressures accurately over a limited range of temperatures, and several ranges must be used to describe a wide range of temperatures. Recently, an equation was reported<sup>1</sup> which describes vapor pressures accurately over the entire vapor pressure curve using only three fluid dependent parameters in addition to the temperatures and pressures at the triple and critical points. A comparison of the new equation with existing vapor pressure equations is provided in Reference 1, therefore it is not repeated here.

This work reports the application of the Iglesias equation to a variety of fluids which are important to the refrigeration and air conditioning industry, and for which experimental measurements have been reported in the literature. The fluid dependent parameters have been determined for several hydrocarbon and halocarbon substances, and minor adjustments have been made to the triple and critical point pressures (within the accuracy of the reported measurements) to provide the best descriptions of the experimental measurements for each fluid. The parameters described in this work are incorporated into a computer program which computes vapor pressures using the Iglesias equation. The program is structured in such a way that parameters for new substances may be added easily, or the existing parameters for substances already in the data bank may be changed easily. The general characteristics of this program are described below.

## VAPOR PRESSURE EQUATION.

The Iglesias vapor pressure equation is based upon a method proposed by Churchill and Usagi<sup>2,3</sup> for correlation development which is very useful if the asymptotic behavior of the function is known at the ends of the range of variables. For the case of the vapor pressure, the asymptotic behavior near the triple and critical points each are known, and according to the Churchill-Usagi approach, they are combined according to

$$p(t) = \left[ [p_0(t)]^N + [p_\infty(t)]^N \right]^{1/N} \quad (1)$$

where the subscripts 0 and  $\infty$  denote the asymptotic limits approaching the triple and critical points respectively. The reduced pressures and temperatures are given by

$$t = \frac{T - T_t}{T_c - T_t} \quad (2)$$

and

$$p = 1 + \frac{P^0 - P_t}{P_c - P_t} \quad (3)$$

so that  $0 < t < 1$  and  $1 < p < 2$ . The asymptote approaching the triple point is

$$p_0(t) = a_0 + a_1 [a_3 t + 1]^{b_0/R} \exp\left(\frac{-a_2 + b_0/R}{a_3 t + 1}\right) \quad (4)$$

where

$$a_0 = 1 - \frac{P^\sigma}{P_c - P_t}$$

$$a_1 = -(a_0 - 1) \exp(a_2 - b_0/R)$$

$$a_2 = b_1/RT$$

$$a_3 = \frac{T_c - T}{T_t}$$

This result is obtained by application of the Clausius-Clapeyron equation and the assumption that the enthalpy of vaporization varies linearly with temperature. Details of the derivation are provided in Reference 1. Because of the relations between the parameters, the fluid-dependent parameters for this asymptote are  $b_0$  and  $b_1$ .

The asymptote approaching the critical point is derived from the assumption of scaling and simple background terms (see reference 1 for details) to be

$$p_\infty(t) = 2 - a_4(1-t) + a_5(1-t)^{2-\theta} + a_6(1-t)^3 + a_7(1-t)^4 \quad (5)$$

Simple relations also exist<sup>1</sup> which give the parameters  $a_5$ ,  $a_6$  and  $a_7$  in Equation (5) in terms of  $a_4$ . These have been determined empirically to be

$$a_5 = -0.11599104 + 0.29506258 a_4^2 - 0.00021222 a_4^5$$

$$a_6 = -0.01546028 + 0.08978160 a_4^2 - 0.05322199 a_4^3$$

$$a_7 = 0.05725757 - 0.06817687 a_4 + 0.00047188 a_4^5$$

Therefore only  $a_4$  in Equation (5) remains as a fluid-dependent fit parameter.

Walton, *et al.*<sup>4</sup>, suggest that  $\theta = 0.199$  provides the optimal representation of experimental data. Therefore, although scaling theory suggests that the value should be lower, we use  $\theta = 0.2$  for this work. Finally, Iglesias-Silva, *et al.*<sup>1</sup>, showed that the empirical exponent  $N$  may be calculated from the reduced triple point temperature according to

$$N = 87 T_t/T_c \quad (6)$$

Finally, only  $a_4$ ,  $b_0$  and  $b_1$  remain as parameters which must be determined from vapor pressure data for each fluid.

## FITTING PROCEDURE

The parameters were determined using standard nonlinear statistical procedures in the form available in the PC-SAS statistical package. The optimal representation occurs when the measurements are weighted statistically to reflect the inaccuracies of the experimental measurements. The parameters are chosen by minimizing the sum of the weighted squares of the differences between the calculated and observed values:

$$SS = \sum_{i=1}^m W_i (\Delta p_i)^2 \quad (7)$$

Two methods were considered for this work. One is that given by Hust and McCarty<sup>5</sup>

$$W_i = \left[ \sigma_i^2(P) + \left( \frac{dP}{dT} \right)^2 \sigma_i^2(T) \right]^{-1} \quad (8)$$

and the other is due to Hall and Waxman<sup>6</sup>

$$W_i = \left[ \sigma_i(P) + \left( \frac{dP}{dT} \right) \sigma_i(T) \right]^{-2} \quad (9)$$

We compared results obtained using Equations (8) and (9) for several substances. No significant differences were observed, so we chose to use the Hall-Waxman method. The variances are calculated from the estimated inaccuracies in the experimental measurements.

Application of either Equation (8) or (9) requires the calculation of the derivative of the vapor pressure with respect to temperature. Because only modest accuracy is required, these values are calculated by first fitting an Antoine equation to the experimental data, then using the resulting Antoine constants to calculate temperature derivatives during the fitting of the Iglesias equation.

## RESULTS

The critical and triple point values used for these fits are listed in Table 1. These originally were obtained from the literature, but some pressures have been adjusted slightly (within the experimental uncertainty of each) to provide better agreement in the fits. For cases where triple point values are not available, the freezing point provides a very good reference point, because there usually is little difference between the freezing and triple point temperatures. The parameters  $a_4$ ,  $b_0$  and  $b_1$  were determined for the light hydrocarbons (methane through butane) and for those halocarbons where sufficient experimental measurements were available from the archival literature to provide a legitimate fit of the parameters. The resulting values are listed in Table 2 along with the averages of the absolute values of the deviations between the experimental values and those calculated from the equation. Table 2 also identifies the data sources for each fluid.

Table 1. Critical and triple point values used for fits

| Species          | Formula   | $T_c$ / K | $P_c$ / kPa | $T_t$ / K | $P_t$ / kPa             |
|------------------|---|-----------|-------------|-----------|-------------------------|
| Methane          | CH <sub>4</sub>   | 190.551   | 4599.2      | 90.685    | 11.696                  |
| Ethane           | CH <sub>3</sub> CH <sub>3</sub>                                 | 305.33    | 4871.4      | 90.348    | 0.0011308               |
| Propane          | CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>                 | 369.85    | 4247.46     | 85.470    | 1.670×10 <sup>-7</sup>  |
| <i>i</i> -Butane | C(CH <sub>3</sub> ) <sub>3</sub>                                | 407.85    | 3640.       | 113.55    | 1.9481×10 <sup>-5</sup> |
| <i>n</i> -Butane | CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub> | 425.16    | 3796.       | 134.86    | 6.7352×10 <sup>-4</sup> |
| R-11             | CFCl <sub>3</sub>   | 471.15    | 4487.1      | 162.15    | 0.0063                  |
| R-12             | CF <sub>2</sub> Cl <sub>2</sub>                                 | 384.95    | 4124.       | 115.19    | 0.00023                 |
| R-22             | CHF <sub>2</sub> Cl <sub>2</sub>                                | 369.30    | 4988.       | 113.      | 0.00024                 |
| R-23             | CHF <sub>3</sub>  | 299.30    | 4858.       | 113.2     | 0.025                   |
| R-32             | CHF <sub>2</sub> F <sub>2</sub>                                 | 351.56    | 5828.       | 137.      | 0.056                   |
| R-123            | CHCl <sub>2</sub> CF <sub>3</sub>                               | 456.87    | 3668.       | 166.      | 0.0055                  |
| R-134a           | CH <sub>2</sub> FCF <sub>3</sub>                                | 374.51    | 4056.       | 172.      | 0.56                    |
| R-141b           | CFCl <sub>2</sub> CH <sub>3</sub>                               | 477.35    | 4250.       | 163.      | 0.0029                  |
| R-142b           | CF <sub>2</sub> ClCH <sub>3</sub>                               | 410.29    | 4041.       | 142.      | 0.014                   |
| R-143a           | CF <sub>3</sub> CH <sub>3</sub>                                 | 346.25    | 3811.       | 161.82    | 1.18                    |
| R-152a           | CHF <sub>2</sub> CH <sub>3</sub>                                | 386.44    | 4520.       | 156.      | 0.100                   |

Typical deviations between the experimental and calculated values are shown in Figures 1, 2 and 3, which show the results for R-32, R-134a and R-152a, respectively. The first, R-32, is representative of the case where only one set of measurements (of moderate quality) have been reported. For R-134a, four sets of values have been reported, and two sets were available for R-152a at the time of fitting. For both R-134a and R-152a, the data are of high quality. All three figures show that the equation is quite capable of describing the entire vapor pressure range to within the estimated experimental uncertainties.

## COMPUTER PROGRAM

Because of the complexity of the equations, we prepared a computer program to calculate vapor pressures according to the Iglesias equation. This program has capability for easy alteration of existing parameters or the addition of parameters for additional fluids as they become available through future statistical treatment and as more experimental values are reported in the literature. The capability for additions or changes is password protected, so that alterations may be controlled and recorded even though a particular copy of the program may have many users.

The current version of the program operates under MS/DOS on PC-compatible machines. It is menu driven and has the capability to provide vapor pressures at single specific temperatures, or to generate tables where the upper and lower bounds and intervals in temperature are specified. Output may be received on the screen, as

printed hard copy, or written to a file on disk. Additional information about the program may be obtained by contacting the corresponding author.

Table 2. Fit parameters and goodness of fit

| Species          | Reference | $a_4$    | $b_0$      | $b_1$     | AAPE <sup>a</sup> |
|------------------|-----------|----------|------------|-----------|-------------------|
| Methane          | 6         | 3.159535 | -19.77081  | 8812.417  | 0.03              |
| Ethane           | 7         | 4.581460 | -36.42229  | 17877.435 | 0.07              |
| Propane          | 8         | 5.205689 | -43.50273  | 24771.221 | 0.07              |
| <i>i</i> -Butane | 9         | 4.999256 | -47.83018  | 28197.481 | 0.54              |
| <i>n</i> -Butane | 10        | 4.797703 | -43.85128  | 28605.450 | 0.51              |
| R-11             | 11        | 4.620788 | -42.98908  | 30789.076 | 0.03              |
| R-12             | 12-13     | 4.840123 | -44.25981  | 25594.772 | 0.06              |
| R-22             | 14-16     | 4.919967 | -45.35556  | 25645.692 | 0.09              |
| R-23             | 17-21     | 4.563538 | -44.54006  | 20546.185 | 0.26              |
| R-32             | 22        | 5.543935 | -40.59925  | 23775.126 | 0.22              |
| R-123            | 23        | 4.703437 | -46.74315  | 32619.809 | 0.18              |
| R-134a           | 24-27     | 4.114466 | -42.47784  | 25799.300 | 0.18              |
| R-141b           | 28        | 4.697202 | -48.00818  | 32769.259 | 0.03              |
| R-142b           | 29-30     | 4.848964 | -8.64520   | 23114.129 | 0.32              |
| R-143a           | 29, 31    | 3.966619 | -31.40464  | 21960.191 | 0.35              |
| R-152a           | 32-33     | 4.425394 | -34.613687 | 25294.458 | 0.06              |

<sup>a</sup>AAPE = average absolute value of percentage deviation of experimental measurements from the best fit equation

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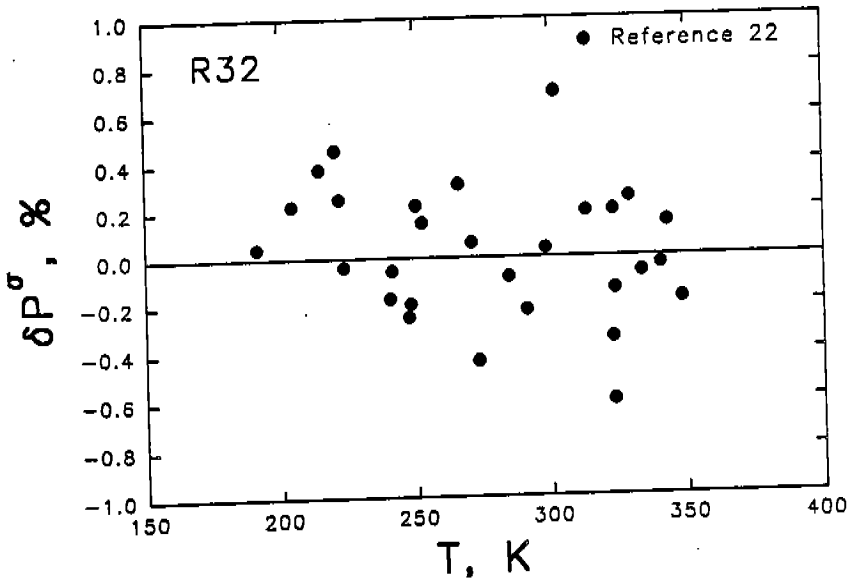


Figure 1. Differences between experimental and calculated vapor pressures for R-32

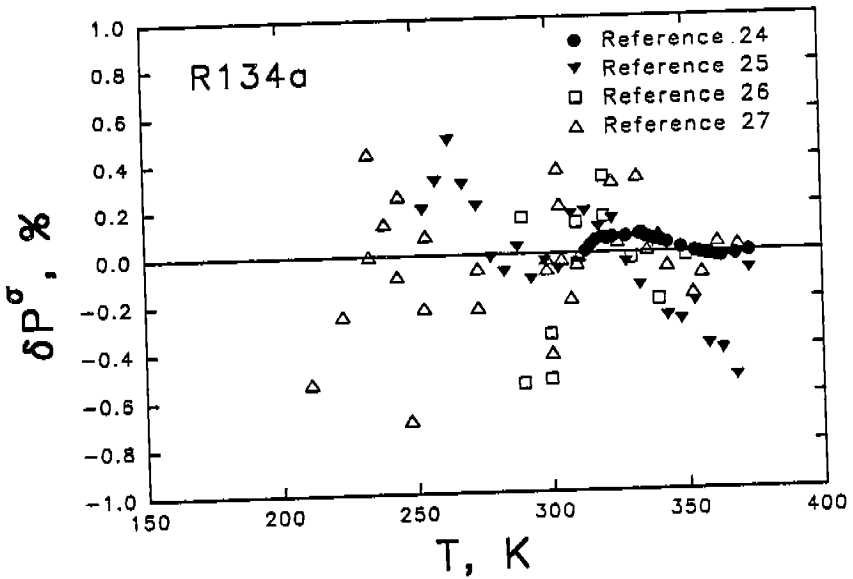


Figure 2. Differences between experimental and calculated vapor pressures for R-134a

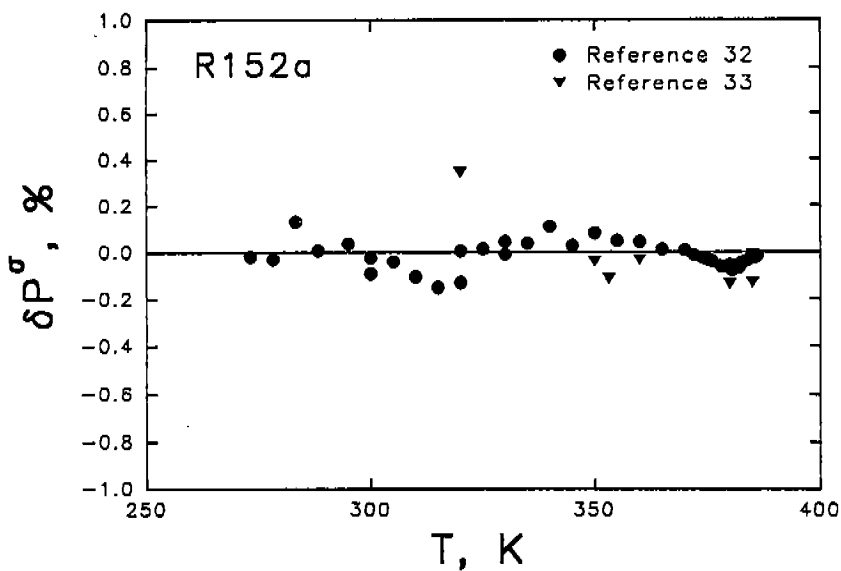


Figure 3. Differences between experimental and calculated vapor pressures for R-152a