

ITS-90 FORMULATIONS FOR VAPOR PRESSURE, FROSTPOINT TEMPERATURE, DEWPOINT TEMPERATURE, AND ENHANCEMENT FACTORS IN THE RANGE -100 TO $+100$ C

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Abstract: With the change in the temperature scale of ITS-90, new temperature dependent equations were required which predict saturation vapor pressure over water and ice, enhancement factor over water and ice, frostpoint temperature, and dewpoint temperature. Internationally recognized formulas based on the previous temperature scale, viewed as self-consistent data sets for vapor pressures and enhancement factors, were chosen as initial defining equations. These formulas, coupled with those defining the temperature difference between the two scales, were used to compute new data sets consistent with the temperature scale of ITS-90. These new data sets were then fitted to equations of the original form, yielding new ITS-90 compatible coefficients to the familiar vapor pressure and enhancement factor equations. In addition, the resulting vapor pressure equations were used to produce a set of inverse approximating equations to yield frostpoint and dewpoint temperatures when the vapor pressure is known. The resulting coefficients, equations, and the conversion methods that produced them are presented.

Keywords: ITS-90, saturation vapor pressure, enhancement factor, frostpoint, dewpoint

1 INTRODUCTION

Prior to establishment of the temperature scale of ITS-90, humidity related quantities were generally computed with respect to the IPTS-68 temperature scale, and continue to be in many cases even well after the adoption of ITS-90. With a maximum deviation between IPTS-68 and ITS-90 of only 26 mK over the range of -100 to $+100^{\circ}\text{C}$, continued use of IPTS-68 equations does seem to have merit. For instance, when computing percent relative humidity (%RH), it is computed from a ratio of vapor pressures within relatively close proximity to one another. So the end results, when computed on one temperature scale versus the other, are of negligible difference. However, when the use of these ratios is not involved, and as humidity generation and measurement techniques become inherently more precise, the need arises for humidity parameters to be more closely matched to the new temperature scale.

While others have generated equations for vapor pressures and enhancements factors on ITS-90, the intent here is not to contradict or negate these prior works. Rather, the purpose is to augment those works with the addition of a consistent set of equations of the exact same form as the IPTS-68 originals, with equivalent useable ranges and comparable accuracies to their IPTS-68 counterparts. This process involved converting a series of ITS-90 temperatures to their IPTS-68 equivalents, computing vapor pressures and enhancement factors using existing IPTS-68 equations, then pairing the results with the original ITS-90 temperatures. The paired data was curve fit to equations of the IPTS-68 form to generate the corresponding ITS-90 coefficients. In addition to determining these new coefficients, new formulas used to predict frostpoint and dewpoint from vapor pressure were also generated.

2 TEMPERATURE CONVERSION BETWEEN ITS-90 AND IPTS-68

The defining equation chosen for conversion of temperatures between the ITS-90 and IPTS-68 scales was that of Rusby¹. Depicted here as equation 1, it covers the range of -189 to $+630^{\circ}\text{C}$, with a stated accuracy of approximately ± 1.5 mK below 0°C and ± 1 mK above 0°C .

$$t_{90} - t_{68} = \sum_{i=1}^8 b_i (t_{90} / 630)^i \quad (1)$$

where t_{90} is temperature in $^{\circ}\text{C}$ on the ITS-90 scale
and t_{68} is temperature in $^{\circ}\text{C}$ on the IPTS-68 scale

with coefficients

$$b_1 = -0.148759$$

$$b_2 = -0.267408$$

$$b_3 = 1.080760$$

$$b_4 = 1.269056$$

$$b_5 = -4.089591$$

$$b_6 = -1.871251$$

$$b_7 = 7.438081$$

$$b_8 = -3.536296$$

3 SATURATION VAPOR PRESSURE

While there have been several vapor pressure equations written over the years on the IPTS-68 temperature scale, those of Wexler^{2,3} have gained the largest international acceptance. In fact, many of the other equations written have been limited range simplifications based on the data from Wexler's formulations. With the assumption that the Wexler equations are considered to be self-consistent data sets on the IPTS-68 temperature scale, his equations were chosen as the basis for conversion to ITS-90.

3.1 Saturation Vapor Pressure over Water

Wexler's² equation 15 (shown here as equation 2) was utilized as the defining formula for saturation vapor pressure over water in the range of 0 to 100°C . Coupled with equation 1 above, 301 independent values of ITS-90 vapor pressures were computed from -100 to $+200^{\circ}\text{C}$ at 1 degree intervals. The data was then curve fit to Wexler's formula to generate new coefficients consistent with the ITS-90 scale. Since it is a common practice to extrapolate Wexler's formula beyond his intended limits of 0 to 100°C , note that extrapolation was also used in the generation of this new data set. The ITS-90 formulation will therefore exhibit comparable results when used in the extrapolated regions below 0 and above 100°C . Wexler's original formulation and coefficients, along with the new coefficients computed for ITS-90 are

$$\ln e_s = \sum_{i=0}^6 g_i T^{i-2} + g_7 \ln T \quad (2)$$

where e_s is the saturation vapor pressure, in Pa, over water in the pure phase
and T is the temperature in Kelvin

with Wexler's coefficients

$$\begin{aligned} g_0 &= -2.9912729 \times 10^3 \\ g_1 &= -6.0170128 \times 10^3 \\ g_2 &= 1.887643854 \times 10^1 \\ g_3 &= -2.8354721 \times 10^{-2} \\ g_4 &= 1.7838301 \times 10^{-5} \\ g_5 &= -8.4150417 \times 10^{-10} \\ g_6 &= 4.4412543 \times 10^{-13} \\ g_7 &= 2.858487 \end{aligned}$$

and for the new ITS-90 scale

$$\begin{aligned} g_0 &= -2.8365744 \times 10^3 \\ g_1 &= -6.028076559 \times 10^3 \\ g_2 &= 1.954263612 \times 10^1 \\ g_3 &= -2.737830188 \times 10^{-2} \\ g_4 &= 1.6261698 \times 10^{-5} \\ g_5 &= 7.0229056 \times 10^{-10} \\ g_6 &= -1.8680009 \times 10^{-13} \\ g_7 &= 2.7150305 \end{aligned}$$

Curve fit of the above equation with ITS-90 coefficients was performed using equal weighting of each of the data points. However, when rounding the coefficients to the resolution shown, slight graphical adjustment of g_2 and g_3 was required to constrain the vapor pressure at the triple point of water to 611.657 Pa while maintaining minimal error across the range. The maximum deviation of vapor pressures between Wexler's formulation (with proper adjustment of temperature to IPTS-68), and the ITS-90 formulation presented here, is within 0.05 ppm from -100 to 100°C . Since this is more than 2 orders of magnitude below Wexler's stated experimental uncertainties, his estimates of uncertainty remain applicable to this ITS-90 formulation.

3.2 Saturation Vapor Pressure over Ice

Wexler's³ equation 54 (shown below as equation 3) was used as the defining formula for saturation vapor pressure over ice in the range of -100 to 0°C . Coupled with equation 1 given previously, 151 values of ITS-90 vapor pressures were computed from -149.99 to $+0.01^\circ\text{C}$ at 1 degree intervals. The data was then curve fit to Wexler's equation to generate new coefficients consistent with the ITS-90 scale. Wexler's original formulation and coefficients, along with the new coefficients computed for ITS-90 are

$$\ln e_s = \sum_{i=0}^4 k_i T^{i-1} + k_5 \ln T \quad (3)$$

where e_s is the saturation vapor pressure, in Pa, over ice in the pure phase
and T is the temperature in Kelvin

with Wexler's coefficients

$$\begin{aligned} k_0 &= -5.8653696 \times 10^3 \\ k_1 &= 2.224103300 \times 10^1 \\ k_2 &= 1.3749042 \times 10^{-2} \\ k_3 &= -3.4031775 \times 10^{-5} \\ k_4 &= 2.6967687 \times 10^{-8} \\ k_5 &= 6.918651 \times 10^{-1} \end{aligned}$$

and for the new ITS-90 scale

$$\begin{aligned} k_0 &= -5.8666426 \times 10^3 \\ k_1 &= 2.232870244 \times 10^1 \\ k_2 &= 1.39387003 \times 10^{-2} \\ k_3 &= -3.4262402 \times 10^{-5} \\ k_4 &= 2.7040955 \times 10^{-8} \\ k_5 &= 6.7063522 \times 10^{-1} \end{aligned}$$

Curve fit of this equation with ITS-90 coefficients was constrained at the triple point of water by proportional over-weighting of that data point. After rounding of coefficients to the resolution shown, some slight graphical adjustment of k_1 through k_3 was required to obtain a flat error trend, while maintaining the vapor pressure relative to the triple point of water at 611.657 Pa. The maximum deviation of vapor pressures between Wexler's formulation (with proper adjustment of temperature to IPTS-68), and the ITS-90 formulation presented here, is within 0.3 ppm from -100 to 0.01°C . Since this is several orders of magnitude below

Wexler's originally stated estimates of uncertainty, his estimates remain applicable to this ITS-90 formulation.

4 DEWPOINT AND FROSTPOINT FORMULAS

Equations 2 and 3 are easily solved for vapor pressures at any given temperature, namely the dewpoint and frostpoint temperatures. However, if vapor pressure is known with temperature as the unknown desired quantity, the solution immediately becomes complicated and must be solved by iteration. For ease of computation, inverse equations have been developed to yield temperature at a given vapor pressure.

4.1 Dewpoint Formula

Equation 2 with ITS-90 coefficients was used to create a table of 201 data points from -100 to 100°C , at 1 degree intervals. The data was equally weighted and fit to equation 4. Agreement between this dewpoint formula and equation 2 with ITS-90 coefficients is better than 0.3 mK over the range of -100 to 100°C .

$$T_d = \frac{\sum_{i=0}^3 c_i (\ln e_s)^i}{\sum_{i=0}^3 d_i (\ln e_s)^i} \quad (4)$$

where T_d is dewpoint temperature in Kelvin
and e_s is the saturation vapor pressure in Pa

with coefficients

$$\begin{aligned} c_0 &= 2.0798233 \times 10^2 \\ c_1 &= -2.0156028 \times 10^1 \\ c_2 &= 4.6778925 \times 10^{-1} \\ c_3 &= -9.2288067 \times 10^{-6} \\ d_0 &= 1 \\ d_1 &= -1.3319669 \times 10^{-1} \\ d_2 &= 5.6577518 \times 10^{-3} \\ d_3 &= -7.5172865 \times 10^{-5} \end{aligned}$$

4.2 Frostpoint Formula

Equation 3 with ITS-90 coefficients was used to create a table of 161 data points from -150 to 10°C , at 1 degree intervals. The data was equally weighted and fit to equation 5. Agreement between this dewpoint formula and equation 3 with ITS-90 coefficients is better than 0.1 mK over the range of -150 to 0.01°C .

$$T_f = \frac{\sum_{i=0}^2 c_i (\ln e_s)^i}{\sum_{i=0}^3 d_i (\ln e_s)^i} \quad (5)$$

where T_f is frostpoint temperature in Kelvin
and e_s is the saturation vapor pressure in Pa

with coefficients

$$\begin{aligned} c_0 &= 2.1257969 \times 10^2 \\ c_1 &= -1.0264612 \times 10^1 \\ c_2 &= 1.4354796 \times 10^{-1} \\ d_0 &= 1 \\ d_1 &= -8.2871619 \times 10^{-2} \\ d_2 &= 2.3540411 \times 10^{-3} \\ d_3 &= -2.4363951 \times 10^{-5} \end{aligned}$$

5 ENHANCEMENT FACTORS

The effective saturation vapor pressure over water or ice in the presence of other gases differs from the ideal saturation vapor pressures given in equations 2 and 3. The effective saturation vapor pressure is related to the ideal by

$$e'_s = e_s f \quad (6)$$

where e'_s is the 'effective' saturation vapor pressure
 e_s is the ideal saturation vapor pressure (as given in equation 2 or 3)
and f is the enhancement factor.

Hyland⁴ gave numeric values and an extensive equation for prediction of the enhancement factor at various temperature and pressure conditions. Greenspan⁵ utilized the data and equations of Hyland to fit the enhancement factor to a more simplified equation, the form of which is due to Goff and Gratch⁶ given as

$$f = \exp \left[\mathbf{a} \left(1 - \frac{e_s}{P} \right) + \mathbf{b} \left(\frac{P}{e_s} - 1 \right) \right] \quad (7)$$

$$\text{with } \mathbf{a} = \sum_{i=0}^3 A_i t^i \quad (8)$$

$$\text{and } \ln \mathbf{b} = \sum_{i=0}^3 B_i t^i \quad (9)$$

where f is the enhancement factor
 e_s is the ideal saturation vapor pressure (as given in equation 2 or 3)
 P is pressure in the same units as e_s
 t is temperature in °C
and A_i, B_i depend on temperature range and are given in the following sections.

5.1 Enhancement Factors for Water, -50 to 100°C

Greenspan used two equations to obtain enhancement factors for water. One applies for temperatures between -50 and 0°C, while the other is used from 0 to 100°C. Equations 8 and 9 with the appropriate IPTS-68 coefficients for the temperature range, coupled with equation 1, were used to generate **a** and **b** data sets for each of the ranges at 1 degree increments. The original coefficients, along with those for ITS-90 in °C and K, are listed below.

For Water -50 to 0°C

IPTS-68 [°C]	ITS-90 [°C]	ITS-90 [K]
$A_0 = 3.62183 \times 10^{-4}$	$A_0 = 3.62183 \times 10^{-4}$	$A_0 = -5.5898101 \times 10^{-2}$
$A_1 = 2.60553 \times 10^{-5}$	$A_1 = 2.6061244 \times 10^{-5}$	$A_1 = 6.7140389 \times 10^{-4}$
$A_2 = 3.86501 \times 10^{-7}$	$A_2 = 3.8667770 \times 10^{-7}$	$A_2 = -2.7492721 \times 10^{-6}$
$A_3 = 3.82449 \times 10^{-9}$	$A_3 = 3.8268958 \times 10^{-9}$	$A_3 = 3.8268958 \times 10^{-9}$
$B_0 = -1.07604 \times 10^1$	$B_0 = -1.07604 \times 10^1$	$B_0 = -8.1985393 \times 10^1$
$B_1 = 6.39725 \times 10^{-2}$	$B_1 = 6.3987441 \times 10^{-2}$	$B_1 = 5.8230823 \times 10^{-1}$
$B_2 = -2.63416 \times 10^{-4}$	$B_2 = -2.6351566 \times 10^{-4}$	$B_2 = -1.6340527 \times 10^{-3}$
$B_3 = 1.67254 \times 10^{-6}$	$B_3 = 1.6725084 \times 10^{-6}$	$B_3 = 1.6725084 \times 10^{-6}$

For Water 0 to 100°C

IPTS-68 [°C]	ITS-90 [°C]	ITS-90 [K]
$A_0 = 3.53624 \times 10^{-4}$	$A_0 = 3.53624 \times 10^{-4}$	$A_0 = -1.6302041 \times 10^{-1}$
$A_1 = 2.93228 \times 10^{-5}$	$A_1 = 2.9328363 \times 10^{-5}$	$A_1 = 1.8071570 \times 10^{-3}$
$A_2 = 2.61474 \times 10^{-7}$	$A_2 = 2.6168979 \times 10^{-7}$	$A_2 = -6.7703064 \times 10^{-6}$
$A_3 = 8.57538 \times 10^{-9}$	$A_3 = 8.5813609 \times 10^{-9}$	$A_3 = 8.5813609 \times 10^{-9}$
$B_0 = -1.07588 \times 10^1$	$B_0 = -1.07588 \times 10^1$	$B_0 = -5.9890467 \times 10^1$
$B_1 = 6.32529 \times 10^{-2}$	$B_1 = 6.3268134 \times 10^{-2}$	$B_1 = 3.4378043 \times 10^{-1}$
$B_2 = -2.53591 \times 10^{-4}$	$B_2 = -2.5368934 \times 10^{-4}$	$B_2 = -7.7326396 \times 10^{-4}$
$B_3 = 6.33784 \times 10^{-7}$	$B_3 = 6.3405286 \times 10^{-7}$	$B_3 = 6.3405286 \times 10^{-7}$

5.2 Enhancement Factors for Ice, -100 to 0°C

To obtain enhancement factors for ice in the range of -100 to 0°C, Greenspan provided 3 equations. One was for the temperature range -100 to -50°C, one was for the temperature range -50 to 0°C, and the final one was somewhat less accurate than the other two but covers the entire range of -100 to 0°C. Again, equations 8 and 9, coupled with equation 1 and the appropriate IPTS-68 coefficients, were used to generate three sets of ITS-90 data for **a** and **b** at 1 degree intervals. The original coefficients, along with those for ITS-90 in °C and K, are listed below.

For Ice -100 to 0°C

IPTS-68 [°C]	ITS-90 [°C]	ITS-90 [K]
$A_0 = 3.64449 \times 10^{-4}$	$A_0 = 3.64449 \times 10^{-4}$	$A_0 = -6.0190570 \times 10^{-2}$
$A_1 = 2.93631 \times 10^{-5}$	$A_1 = 2.9367585 \times 10^{-5}$	$A_1 = 7.3984060 \times 10^{-4}$
$A_2 = 4.88635 \times 10^{-7}$	$A_2 = 4.8874766 \times 10^{-7}$	$A_2 = -3.0897838 \times 10^{-6}$
$A_3 = 4.36543 \times 10^{-9}$	$A_3 = 4.3669918 \times 10^{-9}$	$A_3 = 4.3669918 \times 10^{-9}$
$B_0 = -1.07271 \times 10^1$	$B_0 = -1.07271 \times 10^1$	$B_0 = -9.4868712 \times 10^1$
$B_1 = 7.61989 \times 10^{-2}$	$B_1 = 7.6215115 \times 10^{-2}$	$B_1 = 7.2392075 \times 10^{-1}$
$B_2 = -1.74771 \times 10^{-4}$	$B_2 = -1.7490155 \times 10^{-4}$	$B_2 = -2.1963437 \times 10^{-3}$
$B_3 = 2.46721 \times 10^{-6}$	$B_3 = 2.4668279 \times 10^{-6}$	$B_3 = 2.4668279 \times 10^{-6}$

For Ice –100 to –50°C

IPTS-68 [°C]

$$\begin{aligned} A_0 &= 9.88896 \times 10^{-4} \\ A_1 &= 5.74491 \times 10^{-5} \\ A_2 &= 8.90422 \times 10^{-7} \\ A_3 &= 6.20355 \times 10^{-9} \\ B_0 &= -1.04148 \times 10^1 \\ B_1 &= 9.11735 \times 10^{-2} \\ B_2 &= 5.14117 \times 10^{-5} \\ B_3 &= 3.55087 \times 10^{-6} \end{aligned}$$

ITS-90 [°C]

$$\begin{aligned} A_0 &= 9.8830022 \times 10^{-4} \\ A_1 &= 5.7429701 \times 10^{-5} \\ A_2 &= 8.9023096 \times 10^{-7} \\ A_3 &= 6.2038841 \times 10^{-9} \\ B_0 &= -1.0415113 \times 10^1 \\ B_1 &= 9.1177156 \times 10^{-2} \\ B_2 &= 5.1128274 \times 10^{-5} \\ B_3 &= 3.5499292 \times 10^{-6} \end{aligned}$$

ITS-90 [K]

$$\begin{aligned} A_0 &= -7.4712663 \times 10^{-2} \\ A_1 &= 9.5972907 \times 10^{-4} \\ A_2 &= -4.1935419 \times 10^{-6} \\ A_3 &= 6.2038841 \times 10^{-9} \\ B_0 &= -1.0385289 \times 10^2 \\ B_1 &= 8.5783626 \times 10^{-1} \\ B_2 &= -2.8578612 \times 10^{-3} \\ B_3 &= 3.5499292 \times 10^{-6} \end{aligned}$$

For Ice –50 to 0°C

IPTS-68 [°C]

$$\begin{aligned} A_0 &= 3.61345 \times 10^{-4} \\ A_1 &= 2.94650 \times 10^{-5} \\ A_2 &= 5.21676 \times 10^{-7} \\ A_3 &= 5.01622 \times 10^{-9} \\ B_0 &= -1.07401 \times 10^1 \\ B_1 &= 7.36812 \times 10^{-2} \\ B_2 &= -2.68806 \times 10^{-4} \\ B_3 &= 1.53964 \times 10^{-6} \end{aligned}$$

ITS-90 [°C]

$$\begin{aligned} A_0 &= 3.61345 \times 10^{-4} \\ A_1 &= 2.9471685 \times 10^{-5} \\ A_2 &= 5.2191167 \times 10^{-7} \\ A_3 &= 5.0194210 \times 10^{-9} \\ B_0 &= -1.07401 \times 10^1 \\ B_1 &= 7.3698447 \times 10^{-2} \\ B_2 &= -2.6890021 \times 10^{-4} \\ B_3 &= 1.5395086 \times 10^{-6} \end{aligned}$$

ITS-90 [K]

$$\begin{aligned} A_0 &= -7.1044201 \times 10^{-2} \\ A_1 &= 8.6786223 \times 10^{-4} \\ A_2 &= -3.5912529 \times 10^{-6} \\ A_3 &= 5.0194210 \times 10^{-9} \\ B_0 &= -8.2308868 \times 10^1 \\ B_1 &= 5.6519110 \times 10^{-1} \\ B_2 &= -1.5304505 \times 10^{-3} \\ B_3 &= 1.5395086 \times 10^{-6} \end{aligned}$$

5.2 Notes Regarding Enhancement Factors

Since the temperature dependency of enhancement factors is very small, little error would be induced by the use of IPTS-68 enhancement factor formulas with ITS-90 temperatures while at low to moderate pressures. However at high pressure, near 2 MPa, the error of this approach is negligible near 0°C, but approaches errors of 15 ppm at –50 and +100°C, and exceeds 50 ppm at –100°C. Although somewhat more significant, these induced errors are still generally more than an order of magnitude lower than Hyland’s original uncertainty estimates. Use of the ITS-90 equations can reduce this systematically induced computation error more than 2 orders of magnitude to within 0.2 ppm over the range –100 to –50°C, 0.05 ppm over the range –50 to 0°C, and within 0.1 ppm over the range 0 to 100°C. Since the use of the ITS-90 formulations prevent any significant additional contribution to the overall computational error, Hyland’s original estimates of uncertainty remain valid.

As an additional note, it is also important to understand that the IPTS-68 enhancement factor formulas of Greenspan were derived using Wexler’s vapor pressure equation for water prior to his 1976 revision, and Goff’s saturation vapor pressure equation for ice based on the temperature scale of 1948. While these IPTS-68 enhancement factor equations apparently remained valid without change up to 1990, even though there were newer equations for the vapor pressures of both water and ice, no attempt was made here to account for these apparent previous discrepancies. The equations presented here for ITS-90 are done so solely in an effort to prevent further degradation of the enhancement formulas from 1990 forward. The goal attempted and accomplished was only that an IPTS-68 enhancement factor computed from an IPTS-68 temperature would yield the same numeric value as an ITS-90 enhancement factor computed from an ITS-90 temperature, when the two temperatures are of the same hotness.

REFERENCES

- 1 Preston-Thomas, H. et al., *Supplementary Information for the International Temperature Scale of 1990*, Bureau International Des Poids Et Mesures (BIPM), December 1990, 1-28
- 2 Wexler, A., *Vapor Pressure Formulation for Water in Range 0 to 100°C. A Revision*, Journal of Research of the National Bureau of Standards – A. Physics and Chemistry, September – December 1976, Vol. 80A, Nos. 5 and 6, 775-785
- 3 Wexler, A., *Vapor Pressure Formulation for Ice*, Journal of Research of the National Bureau of Standards – A. Physics and Chemistry, January – February 1977, Vol. 81A, No. 1, 5-19
- 4 Hyland, R.W., *A correlation for the second interaction virial coefficients and enhancement factors for CO₂-free moist air from –50 to +90°C*, Journal of Research of the National Bureau of Standards – A. Physics and Chemistry, July-August 1975, Vol. 79A, No. 4, 551-560.
- 5 Greenspan, L., *Functional Equations for the Enhancement Factors for CO₂-Free Moist Air*, Journal of Research of the National Bureau of Standards – A. Physics and Chemistry, January-February 1976, Vol. 80A, No. 1, 41-44.
- 6 Goff, J. A., *Standardization of Thermodynamic Properties of Moist Air*, Heating, Piping, and Air Conditioning, 1949, Vol. 21, 118.