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Five Short Equations describing the saturated Density and Enthalpy of Carbon Dioxide (CO₂) Vapor and Liquid

by A.E. for myChemEngmusings.wordpress.com

In this post I will present a set of five short, handy - yet accurate - equations to predict the density and enthalpy of Carbon Dioxide in the saturated liquid and vapor phase. The key, I found, to successfully describe these two physical properties, density and enthalpy, over nearly the entire two phase region is the use of the vapor compressibility factor 'Z', under saturation conditions ('Z_{sat}'), as an extra variable in addition to temperature and pressure.

Such set of short and accurate corresponding states equations of pure CO₂ can be of great help to easy to implement these physical properties in 'spreadsheet or flow-sheet' studies of recovery systems of CO₂ or study of reduction of its releases into the atmosphere.

The compressibility factor of the saturated *vapor* phase, 'Z_{sat}', plays, as said, a key role in describing the *saturated liquid* phase density and *liquid* phase enthalpy of Carbon Dioxide. This surprising role will be demonstrated in the calculation examples (see Part II)!

The five equations presented below have been developed based on the accurate thermophysical properties measured and reported by Span and Wagener, see Ref. 1

The very first short equation to be presented here therefore is the correlation of how 'Z_{sat}' itself relates to saturation pressure or temperature. These five equations described are:

- (a)- the CO₂ saturated *vapor* compressibility factor, symbol: **Z_{sat}**
- (b)- the CO₂ saturated *vapor* density, symbol: **Rho_{vap}**
- (c)- the CO₂ saturated *liquid* density, symbol: **Rho_{liq}**
- (d)- the CO₂ saturated *liquid* enthalpy, symbol: **h_{liq}**
- (e)- the CO₂ saturated *vapor* enthalpy, symbol: **H_{vap}**

This post is long and has therefore been divided into three main parts:

Part I presents the five short equations in sections (a) to (e) .

Part II gives some numerical calculation examples

Part III gives the basis on which these short equations rest.

References

Appendices

App. A: Table with basic thermophysical property data for

Carbon Dioxide , taken from Span and Wagner (ref.1) for easy reference

App. B: Excel Spreadsheet link with short equation verifications

App. C : Graphical representations of the equations (a) to (e) in Part I

Please do note that in this blog the equation formula's presented here are written in an 'excel' style format hence multiplications are shown as ' * ' and raising to the power as '^' and divisions as ' / '. Subscripts have been indicated by an italic part of the variable's symbols.

The predictions made by these five equations are all valid over the same temperature range covering nearly the entire two phase region of CO₂, viz. from 218 to 302 degrees Kelvin : $218 = < T < = 320$.

The average relative percentage errors in the predictions made by each of these five equations for Carbon Dioxide over this temperature range are quoted in the text accompanying each equation described here below.

Note that all enthalpy values for the two phase region listed by Span & Wagner (ref.1) have been rescaled such that the liquid enthalpy of Carbon Dioxide at the Triple Point is set to Zero and hence the vapor phase enthalpy at the Triple Point is equal to its heat of evaporation.

A pdf version of this post is found here:

text starts next page

Part I -- The Five Short Equations

Part I -(a) The Saturated CO2 Vapor Compressibility Factor 'Zsat'

Along the saturation curve the temperature and pressure are coupled via the vapor pressure relationship. Therefore the saturated vapor compressibility factor 'Zsat' can be expressed either as function of the saturation pressure or as function of the saturation temperature. The 'Zsat' factor is given here both as a function of pressure (labeled 'ZsatP') as well as a function of temperature (labeled 'ZsatT') as shown below:

$$\mathbf{ZsatP = 1 - 0.03543 * P^{0.689} / (73.773 - P)^{0.076}}$$

In this equation 'ZsatP' = the saturated vapor compressibility factor for CO2 and 'P' = the absolute (saturation) pressure in Bar abs.

This equation covers the absolute pressure range from 5.504 Bar abs. to 70.267 Bar abs , corresponding to saturation temperatures from 218 to 302 deg.Kelvin !

This equation allows you to calculate the 'Zsat' factor with an average percentage error of 0.14% compared to Span & Wagner's measured data (Ref.1).

Alternatively, 'Zsat' can be expressed as a unique function of the absolute saturation temperature as follows:

$$\mathbf{ZsatT = 1 + 0.001613 * (T * (304.128 - T))^{0.6} - 0.67508}$$

This equation allows the 'Zsat' factor to be calculated with an average percentage error of 0.13%! See the graphical representation in diagrams for these two equations in the Appendix.

Part I -(b) The Saturated Vapor Density of CO2 'Rhovap'

The saturated CO2 vapor density 'Rhovap' can be expressed as a function of the saturation temperature. The following short equation shows how 'Rhovap' can be directly calculated as a function of absolute temperature:

$$\mathbf{\ln(Rhovap / Rhoc) = C * (Tc - T)^{0.68} / T^{1.15} / ZsatT^{0.33} + B}$$

in which 'Rhovap' is expressed in kg/m³ ; and Rhoc= 467.6 kg/m³ ; and C= - 75.135 ; and B = -0.1855 ; 'Tc' is the critical temperature of 304.128 deg K ; and 'T' is the absolute temperature in deg.K ; and 'ZsatT' is the value calculated from the equation in the above section I-(a).

The calculation results of this equation predict the saturated density values having an average percentage error of 0.33%.

For the case that you have both *the saturation temperature* and *the saturation pressure* available and known to you, the vapor density can be straightforwardly calculated from the 'Zsat' equations plus the Universal Gas Law. This leads to the following short equation:

$$\mathbf{Rhovap = 529.304 * P / (Zsat * T)}$$

in which 'Rhovap' = density of saturated Carbon Dioxide in kg/m³ ;

'P' = the absolute pressure in Bara ; 'Zsat' = the compressibility factor of saturated CO2 vapor ; 'T' = the vapor absolute temperature in Degrees Kelvin. If for Zsat the values for 'ZsatT' are used the calculated densities have an average percentage error of 0.13 % , else when using 'ZsatP' values it is 0.14% .

Part I -(c) The Density of Saturated Liquid Carbon Dioxide 'Rho_{liq}'

The following equation for predicting the saturated liquid density makes use of the surprising 'find' that it can be correlated with the saturated vapor compressibility 'ZsatT' factor as follows:

$$\mathbf{Rho_{liq} = - 3.53267 * (T - T_o) / (ZsatT^{0.646}) + 1180.409}$$

in which 'Rho_{liq}' is the saturated liquid density in kg/m³ ; 'T' = the absolute temperature in deg.K ; 'T_o' = the triple point temperature of CO₂ of 216.592 deg.K ; and 'ZsatT' is the calculation result of the equation given in I-(a).

The predicted liquid density values have an average percentage error of 0.08 % !

Part I -(d) The saturated Liquid Carbon Dioxide Enthalpy 'h_{liq}'

The enthalpy of saturated liquid Carbon Dioxide can be calculated directly from the following short equation:

$$\mathbf{h_{liq} = 1.90 * (T - T_o) / ZsatT^{0.304}}$$

in which 'h_{liq}' is the enthalpy is expressed in kJ/kg ; ; 'T' = the absolute temperature in deg. K ; 'T_o' = the Carbon Dioxide triple point temperature 216.592 deg.K and 'ZsatT' is the calculation result of the equation in Part I -(a).

This formula predicts the saturated liquid enthalpy with an average percentage error of 0.22%.

Part I -(e) The Saturated Vapor Enthalpy of CO₂ 'H_{vap}'

The enthalpy of saturated CO₂ vapor can be calculated with the following short equation:

$$\mathbf{H_{vap} = 350.376 * ZsatT + 0.9496 * (T - T_o)^{1.1} + 28.413}$$

in which 'H_{vap}' is expressed in units of kJ/kg ; 'ZsatT' = the compressibility factor of saturated CO₂ vapor as function of 'T' as shown in Part I -(a) .

This formula predicts the saturated CO₂ vapor enthalpy values with an average percentage error of 0.16 % .

For the case that you know the saturated pressure (i.e. vapor pressure) in addition to the temperature then the 'ZsatT' value maybe replaced with the 'ZsatP' value upon which this equation will yield an average percentage error of 0.06% !

Part II -- Some Numerical Calculation Examples

Part II -- Some Numerical Examples CO2 Physical Property Calculations

<u>Correlated Properties</u>	<u>---- CONDITIONS ----</u>		<u>PROPERTY VALUES</u>	
	<u>T</u> deg. K	<u>P</u> Bara	<u>-Calculated Value-</u> <u>by Correlations</u>	<u>-Measured Value-</u> <u>Span&Wagner</u>
<i>ZsatP</i>	-----	41.61	0.645	0.646
<i>ZsatT</i>	280	-----	0.645	0.646
<i>Rhovap</i>	280	-----	121.77	121.74
<i>Rhovap</i>	280	41.61	121.9	121.74
<i>Rholiq</i>	280	-----	883.1	883.6
<i>hliq</i>	280	-----	137.7	137.3
<i>Hvap</i>	280	-----	345.5	345.9

see excel spreadsheet

Part III -- The Basis for The Five Short Equations

Part III -(a) The Vapor Compressibility Factor 'Zsat' (ZsatP , ZsatT)

The vapor compressibility factor 'Z' for CO2 under *saturation conditions* can be expressed as a unique function of either the reduced pressure or the reduced temperature. I discovered that by plotting the left hand side of the following equation:

$$(1-Z_{sat}) / (1-Z_c) = A * Pr^n / (1-Pr)^m + B$$

versus the right hand side ratio term in Pr, the four parameters (exponents 'n' and 'm' plus the constants 'A' and 'B') can be determined by linear regression! The left hand side ratio signifies the relative deviation of the 'Z' factor from the ideal gas one. Having determined the four constants, the compressibility factor 'Zsat' as function of the reduced pressure 'Pr' can be written as:

$$Z_{satP} = 1 - (1 - Z_c) * (A * Pr^n / (1 - Pr)^m + B)$$

Upon simplification we get the short equation for 'ZsatP' as shown in Part I -(a).

Alternatively, the saturated compressibility Factor 'Zsat' can be expressed as a unique function of the absolute saturation temperature as follows :

$$(1-Z_{sat}) / (1-Z_c) = A * (Tr * (1-Tr))^n + B$$

from which the four - different- exponents and constants can again be determined by linear regression which gives upon simplification:

$$Z_{sat}T = 1 - (1 - Z_c) * (A * (Tr * (1 - Tr))^n + B)$$

Note that – of course - each of these two equations has a different set of the four parameters. The following values were arrived at:

in the 'ZsatP' equation A= 0.682 ; B= 0 ; n= 0.689 ; and m = 0.076

In the 'ZsaT' equation A= - 2.1214 ; B= 0.9305 ; n= 0.6 and 'm' = 0

With the critical Z value 'Zc' for CO2 equal to 0.2745 (Ref. 1) the two 'Zsat' equations can be simplified as shown in Part I –(a).

Part III -(b) The Saturated CO2 Vapor Density 'Rhovap'

In general the saturated vapor density can be straightforwardly calculated from the Universal Gas Law when the saturation conditions of temperature and pressure as well as the compressibility factor 'Z' are known. In general the vapor density derived from the Universal Gas Law reads:

$$Rhovap = 100 * P * MW / (Z * R * T)$$

with 'Rhovap' in kg/m³ ; pressure 'P' in Bar absolute ; 'MW' is the Molecular Weight of the particular gas ; 'Z' is the compressibility factor ; 'R' is the Universal Gas Constant equal to 8.31451 kJ/ kmol/deg.K ; The factor 100 emerges because the pressure is expressed in Bar (1 Bar = 1000 Pa) and 'T' is the absolute temperature in deg.K.

Applying this formula to Carbon Dioxide we get:

$$Rhovap = 100 / 8.31451 * 44.009 * P / (Z * T) \quad \text{or in short:}$$

$$Rhovap = 529.304 * P / (Z * T)$$

For example let us take the conditions of T and P for saturated conditions given in Part II where 'T' =280 deg.K and 'P' = is 41.6 Bar and the 'Zsat' value of 0.645 we get:

$$Rhovap, sat = 529.304 * 41.6 / (0.645 * 280) = 121.73 \text{ kg/m}^3$$

In summary for the case of knowing *both* the saturation temperature *and* the saturation pressure (= vapor pressure) and having calculated the 'Zsat' value with the help (one of) the 'Zsat' equations in Part I -(a)- the saturated CO2 vapor density can be directly calculated from the short equation as shown.

For the case that only the temperature is known and saturation occurs, the saturated vapor density can be expressed as a unique function of temperature only. Thus it should be possible to correlate the 'Rhovap, sat' directly with the absolute (reduced) temperature. The following corresponding state type correlation was successful in relating 'Tr' and '(1-Tr)' and 'ZsatT' with the saturated vapor density as follows:

$$\ln(\text{Rhovap} / \text{Rhoc}) = A * (\text{Tr}^p * (1-\text{Tr})^q / \text{Zr}^n) + B$$

in which 'Rhoc' is the critical density in kg/m³ ; 'Tr' = reduced temperature and $\text{Zr} = \text{ZsatT} / \text{Zcrit}$ and 'Zc' = 0.2745 .

A linear regression yielded the following constants for CO₂ :

$$p = -1.15 \quad q = 0.68 \quad n = 0.33 \quad A = 0.7836 \quad B = 0.1855$$

Note: the equation implicitly 'encapsulates' the CO₂ vapor pressure relation with temperature!

This equation can be algebraically simplified to:

$$\ln(\text{Rhovap} / \text{Rhoc}) = C * (\text{Tc} - \text{T})^{0.68} / \text{T}^{1.15} / \text{ZsatT}^{0.33} + B$$

with Rhoc = 467.6 kg/m³ and C = -75.135 and B = -0.1855 and Tc = 304.1282 deg.K .
The calculated vapor density has an average percentage error of 0.33% over the temperature range 218 = < T < = 302 .

Part III -(c) The Saturated CO₂ Liquid Density 'Rholiq'

In earlier posts (Ref.2) it has been demonstrated that, for the lower hydrocarbons, an accurate correlation of the saturated liquid density can be developed involving the reduced absolute temperature , Tr, and, surprisingly, the *saturated vapor's compressibility factor*, 'Zsat'.

In this post we are further refining such more general correlation by introducing two new variables namely: 'Theta' to replace 'Tr' and 'Zr' to replace 'Zsat'. These two variables are defined as:

$$\text{Theta} = (\text{T} - \text{To}) / (\text{Tc} - \text{To}) \quad \text{and} \quad \text{Zr} = \text{Zsat} / \text{Zc} .$$

'Theta' can be seen as *the relative liquid temperature progression* across a pure substance's two phase region. 'Zr' stands for the *reduced* saturated compressibility factor with 'Zc' being the critical compressibility factor.

The new corresponding states correlation can be written in terms of 'Theta' and 'Zr' as follows:

$$\text{Rholiq} / \text{Rhoc} = A * \text{Theta}^m / \text{Zr}^n + B$$

A linear regression on the Span & Wagner data for CO₂ yields the following constants:
A = - 1.5244 ; B = 2.5244 ; m = 1.00 ; n = 0.646

Thus, for CO₂ this corresponding states equation reads:

$$\text{Rholiq} / \text{Rhoc} = - 1.5244 * \text{Theta} / \text{Zr}^{0.646} + 2.5244$$

We can write out 'Theta' and 'Zr' out in terms of their definitions:

$$\text{Rholiq} / \text{Rhoc} = - 1.5244 * (\text{T}-\text{T}_0) / (\text{T}_c-\text{T}_0) / (\text{Zsat} / \text{Zc})^{0.646} + 2.5244$$

Next, substituting the physical property constants for CO₂ into this equation with $\text{T}_0 = 216.592 \text{ deg.K}$; $\text{T}_c = 304.1282 \text{ deg.K}$; and $\text{Zc} = 0.2745$ and further algebraically simplifying gives the short equation shown in Part I -(a)

$$\text{Rholiq} = - 3.53267 * (\text{T}-\text{T}_0) / (\text{Zsat}^{0.646}) + 1180.409$$

The relative percentage error in the prediction is 0.08% over nearly the entire two phase region of 218 to 302 degrees Kelvin.

Part III -(d) The Saturated Liquid Enthalpy 'h_{liq}'

The enthalpy of saturated liquid Carbon Dioxide can be written, in analogy with the density, in terms of the same general equation with 'Theta' and 'Zr' as variables as follows:

$$h_{liq} / h_c = A * \text{Theta}^m / \text{Zr}^n + B$$

in which 'h_{liq}' = the saturated liquid enthalpy in units of kJ/kg and 'h_c' = the critical enthalpy. The four constants in this corresponding state correlation have of course different values from the density correlation equation!

For CO₂ a linear regression on the Span & Wagner data yields the following constants:
 $A = 0.977$; $B = 0.0$; $m = 1.00$; $n = 0.304$

Simplifying this equation by substituting the CO₂ physical properties constants gives us as short equation:

$$h_{liq} = 1.90 * (\text{T} - \text{T}_0) / \text{Zsat}^{0.304}$$

The relative percentage error is 0.22% .

Part III -(e) The Saturated CO₂ Vapor Enthalpy 'H_{vap}'

The saturated vapor enthalpy can also be described with the two variables 'Theta' and 'Zr' just as for liquid enthalpy. In a previous post (Ref. 3 of 19 aug 2015) the development of the following equation has been described in detail. It reads:

$$\langle H_{vap} \rangle_{sat} = A * \text{Theta}^m * \text{Zr}^n + B \quad \text{Eq.III e - 1}$$

in which the symbol ' $\langle H_{vap} \rangle_{sat}$ ' stands for :

$$\langle H_{vap} \rangle_{sat} = (H_{vap} - H_o * \text{Zsat}T) / (H_c - H_o * \text{Zc}) \quad \text{Eq.III e -2}$$

Note that this expression (Eq.III e-2) contains two *variables* and three physical properties constants. From combining we find as the general expression for 'Hvap,sat':

$$H_{vap,sat} = H_o * Z_{sat}T + (H_c - H_o * Z_c) * (A * \Theta^m * Z^n + B) \quad \text{Eq.III e -3}$$

This general expression can be applied to pure Carbon Dioxide using the data of Span & Wagner for saturated conditions. The left hand side '<Hvap>sat' expression (Eq.III e-1) is calculated and subjected to a linear regression against the right hand side containing the variables 'Theta' and 'Zr'. This yielded the following four constants: A = 0.833 ; B = 0.1821 ; m = 1.1 ; and n=0.0

Substituting these four 'right hand side' constants :

$$H_{vap,sat} = H_o * Z_{sat}T + (H_c - H_o * Z_c) * (0.833 * \Theta^{1.1} * 1 + 0.1821)$$

Next, upon substituting the physical property constants $H_o = 350.376$ kJ/kg , $H_c = 252.21$ kJ/kg and $Z_c = 0.2745$ we get for the factor $H_c - H_o * Z_c$ the value 156.032 and hence the short equation becomes:

$$H_{vap,sat} = 350.376 * Z_{sat}T + 0.94946 * (T - T_o)^{1.1} + 28.413$$

The average relative percentage error for the calculated values with this equation is 0.16%. Note: if 'ZsatP' is used the average error% shows to become as low as 0.06% !

References.

- (1) Span and Wagner : J.Phys.Chem.Ref.Data, Vol 25,No6,1996, p.1509
- (2) liquid density with Za check ; link to Post dated: Jan 21 , 2015 .
- (3) development post of 19 Aug 2015 ; link to Post dated: Aug 16 , 2015 .

Appendices

App A: Some Carbon Dioxide 's Thermo-Physical Properties :

(taken from Span & Wagner, Ref.1)

Mol. Weight : 44.009 kg/kmol

Triple point : Temperature : $T_o = 216.592$ deg. Kelvin ; Pressure 5.1795 Barabs

Critical Temperature: $T_c = 304.1282$ Deg. K

Critical Pressure: $P_c = 73.773$ Barabs

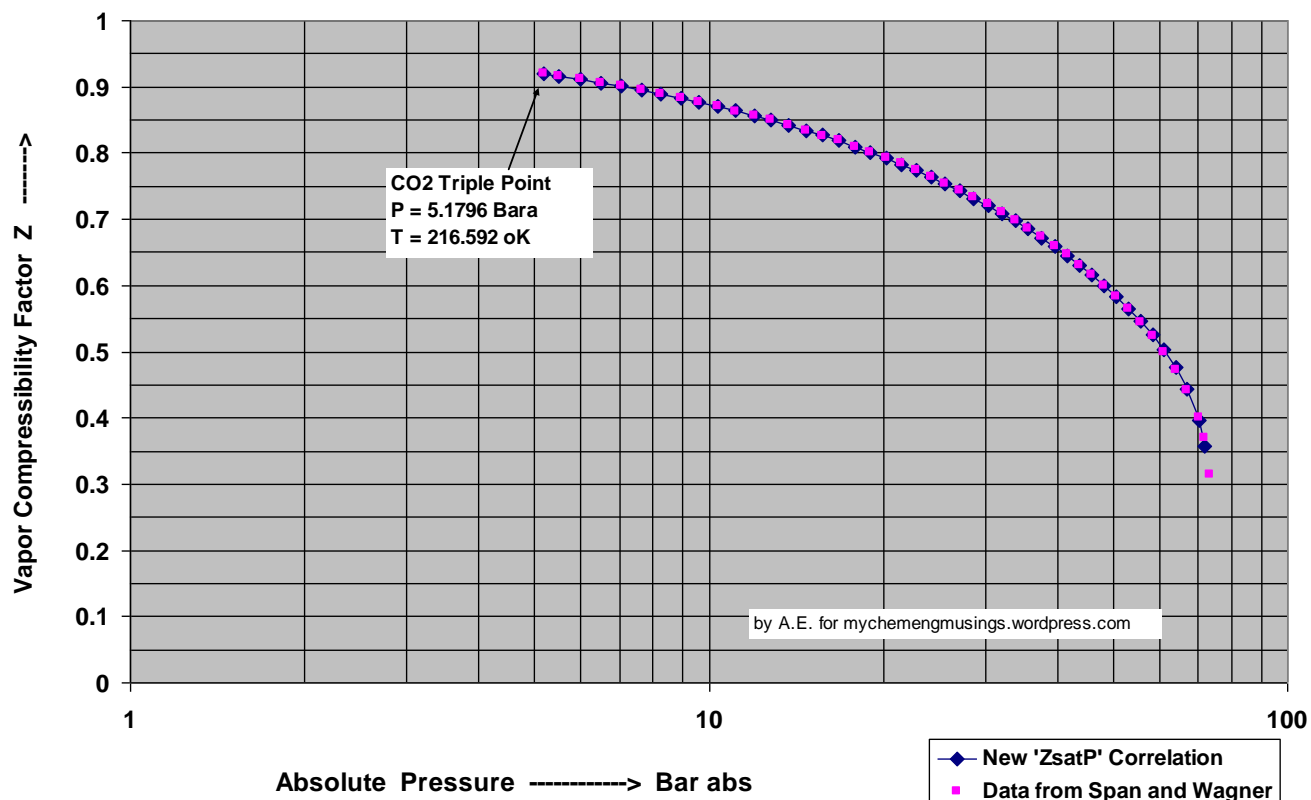
Critical Density: $\rho_{oc} = 467.7$ kg/m³

Critical Compressibility Factor: $Z_c = 0.2745$

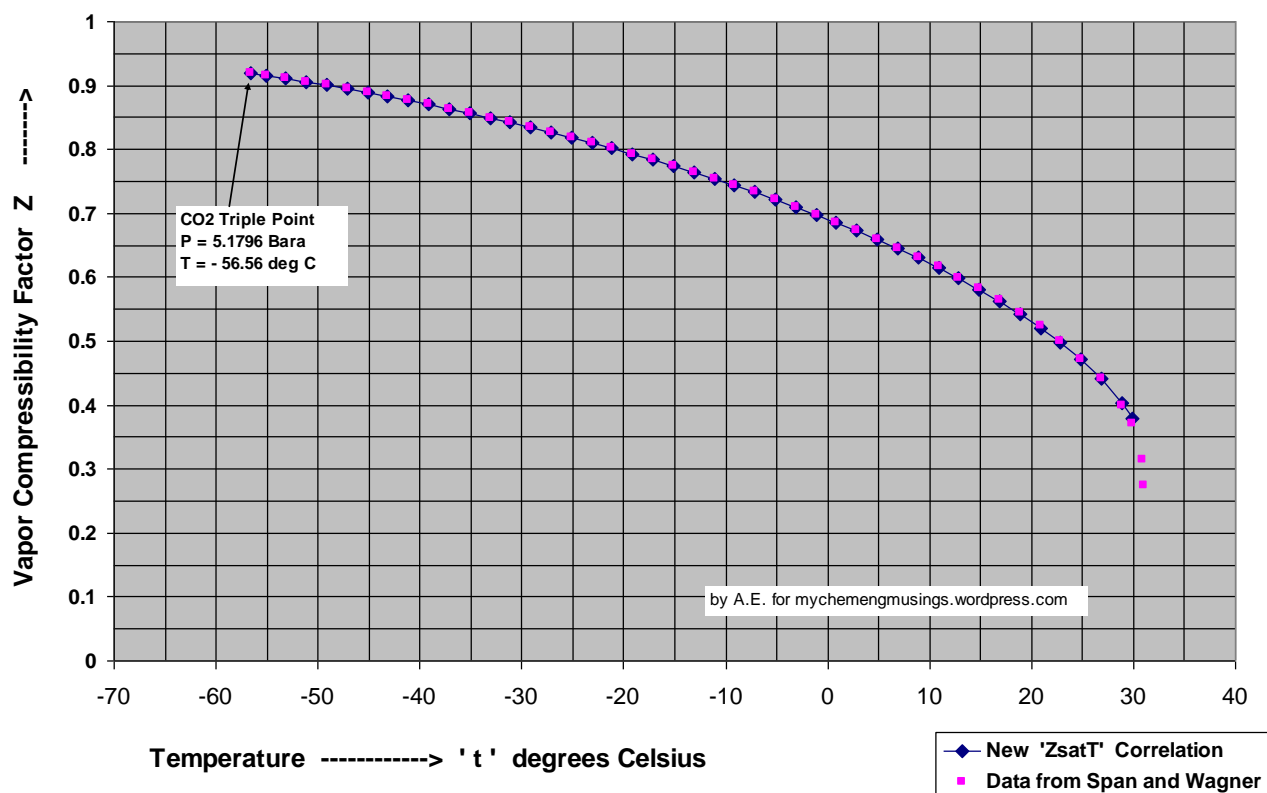
App B: Excel Spreadsheet link with short equation verifications

App C: Graphical representations of the equations (a) to (e) in Part I

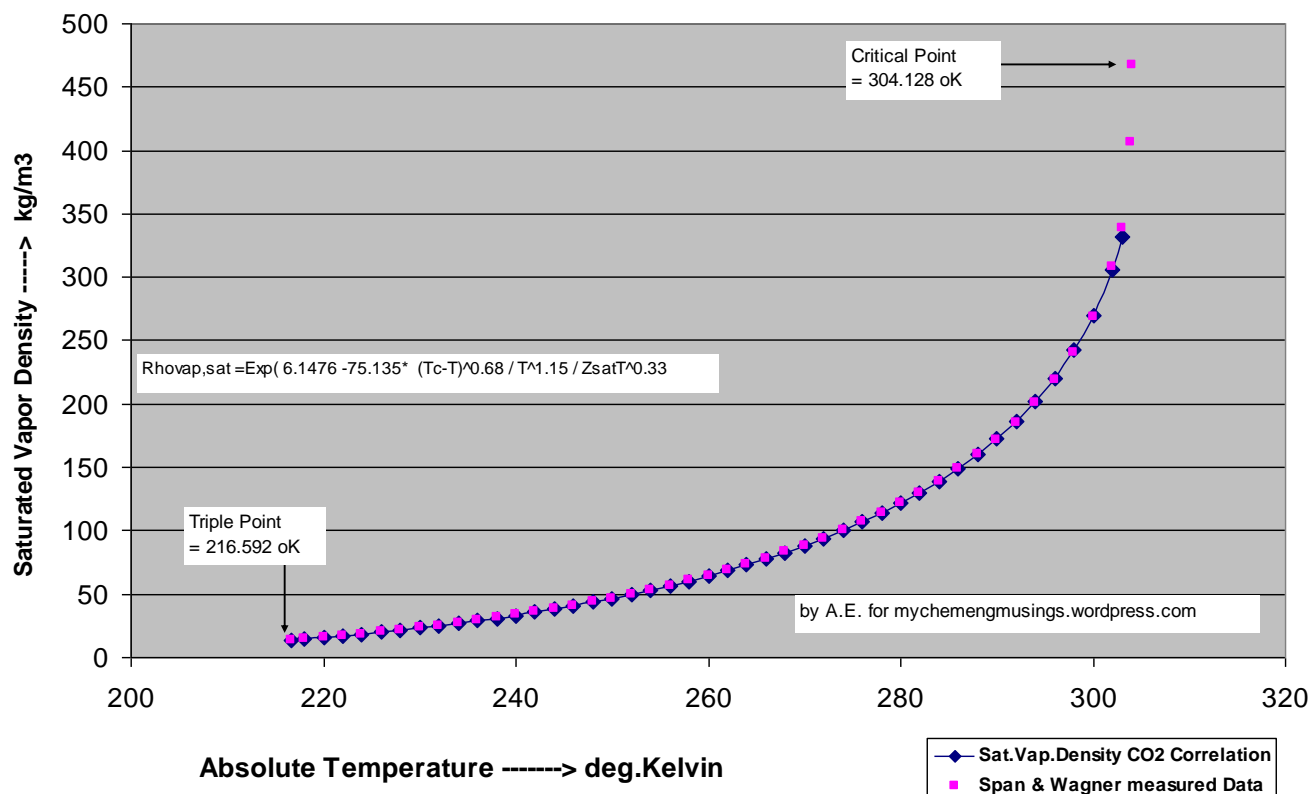
Saturated Carbon Dioxide Vapor Compressibility Factor 'ZsatP' equation versus absolute Pressure



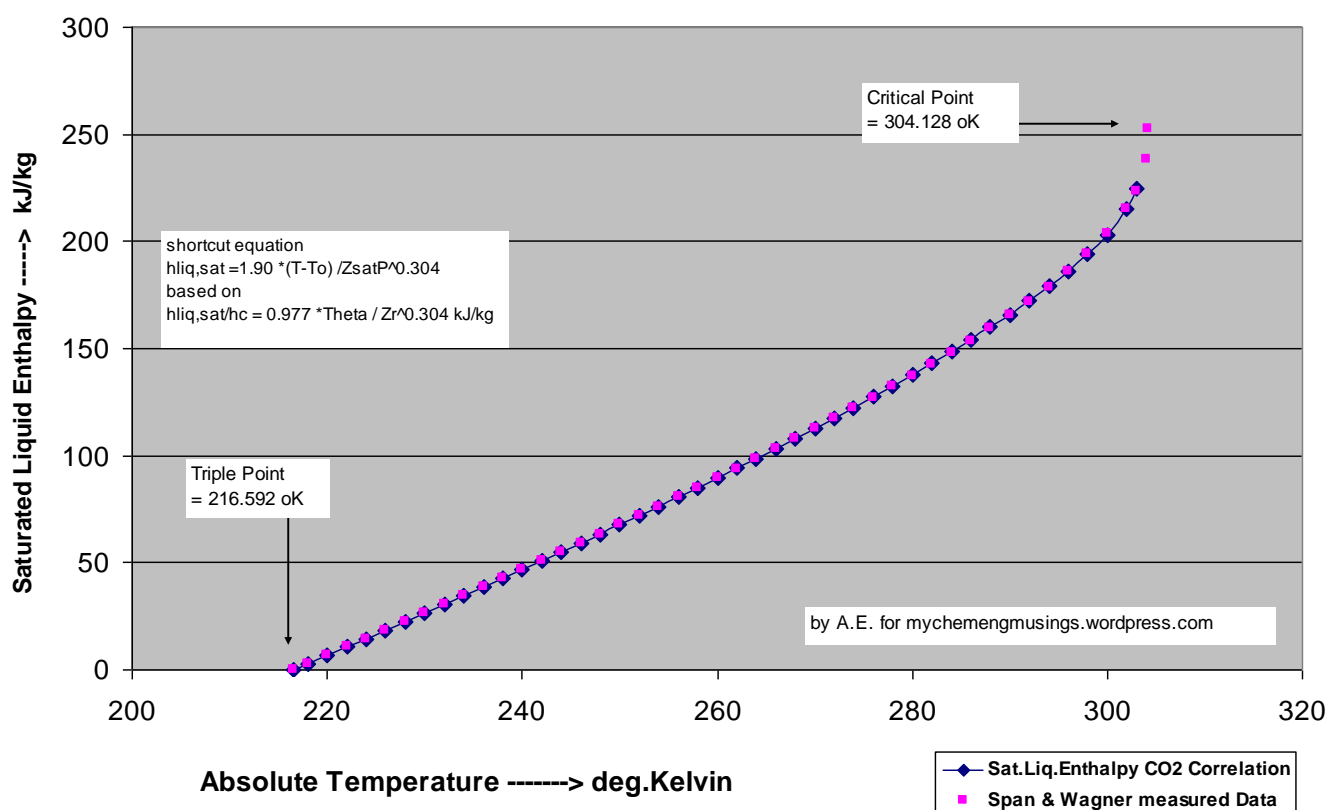
Saturated Carbon Dioxide Vapor Compressibility Factor 'ZsatT' vs Degrees Celsius

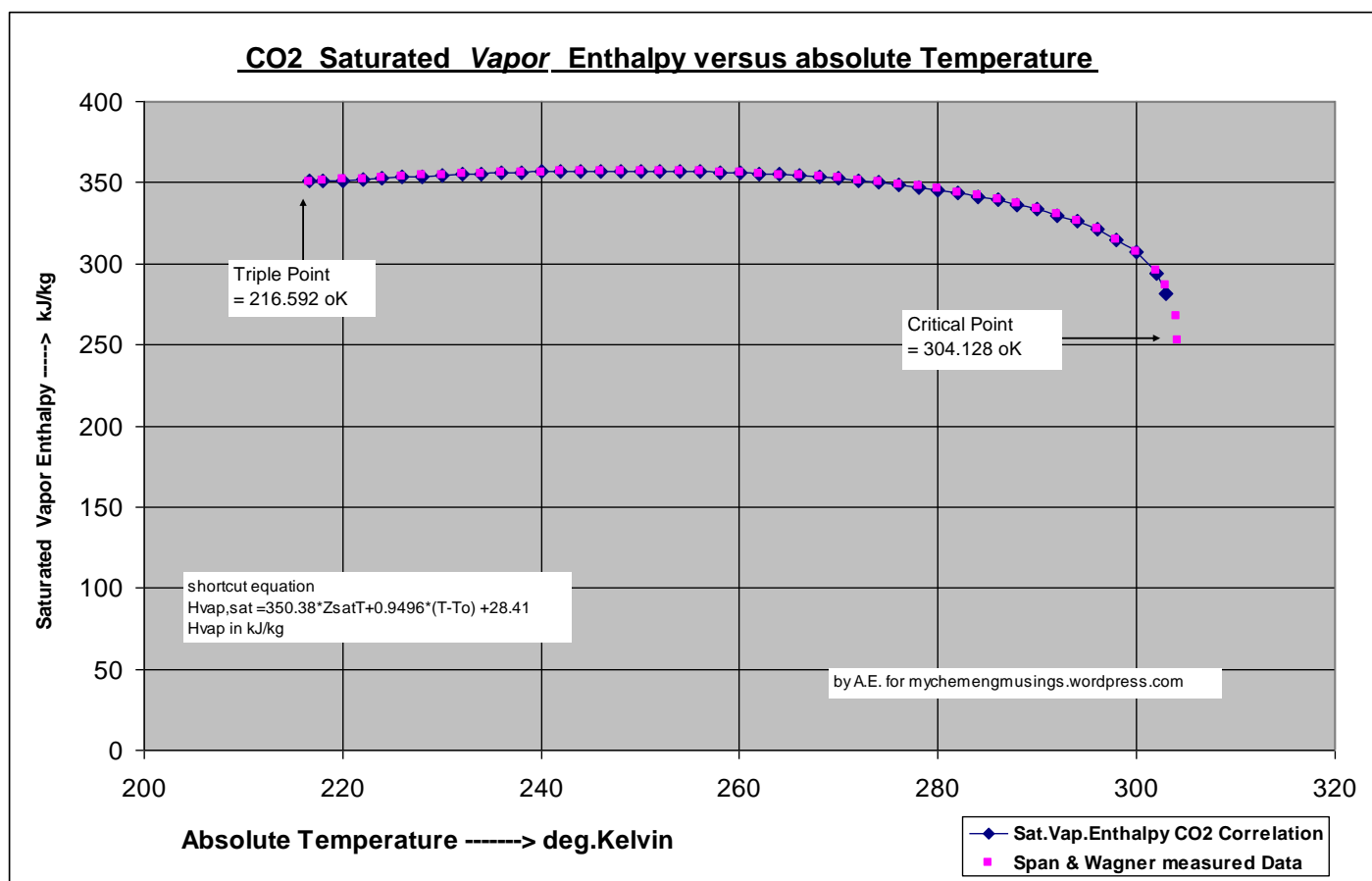
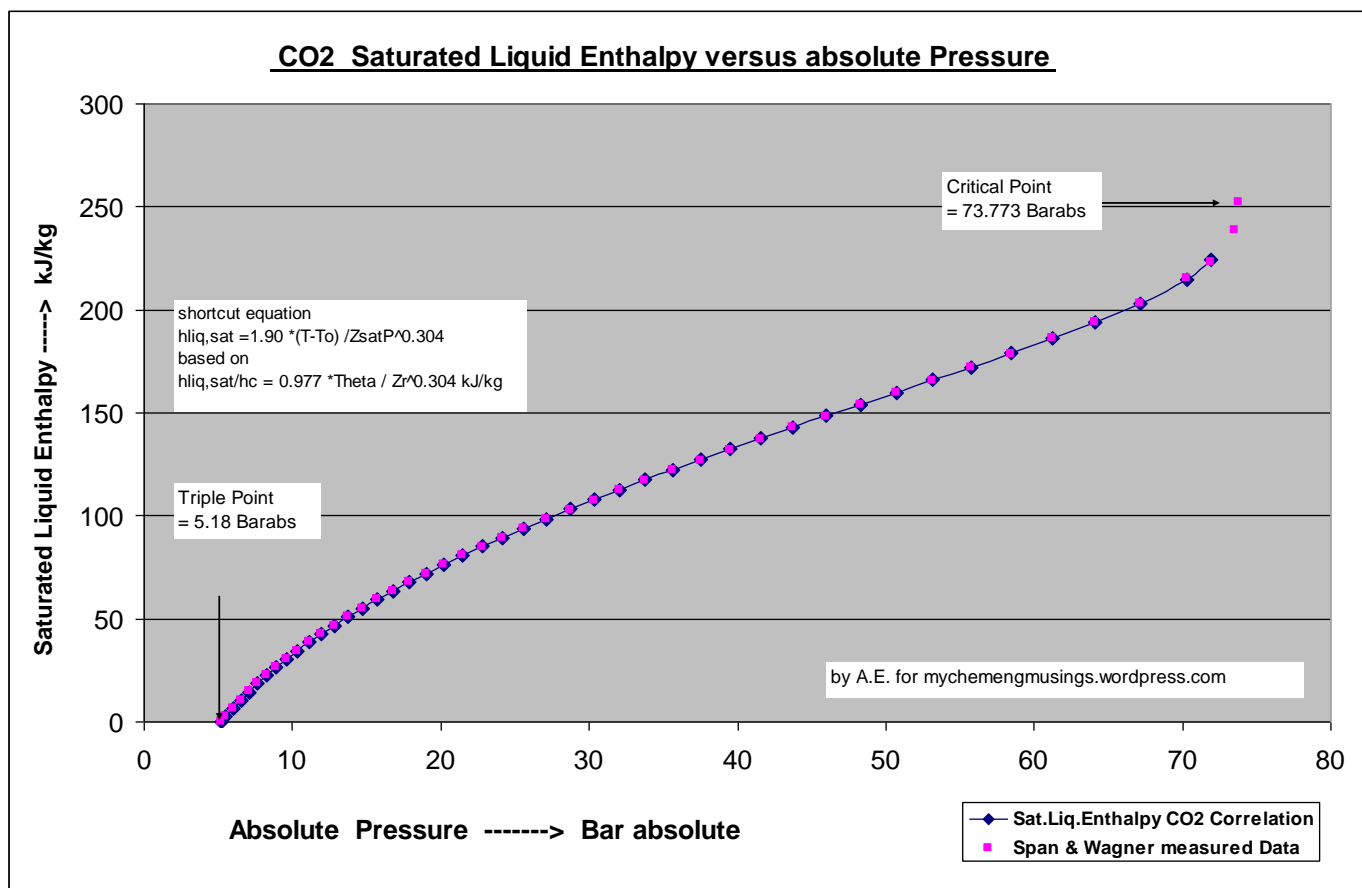


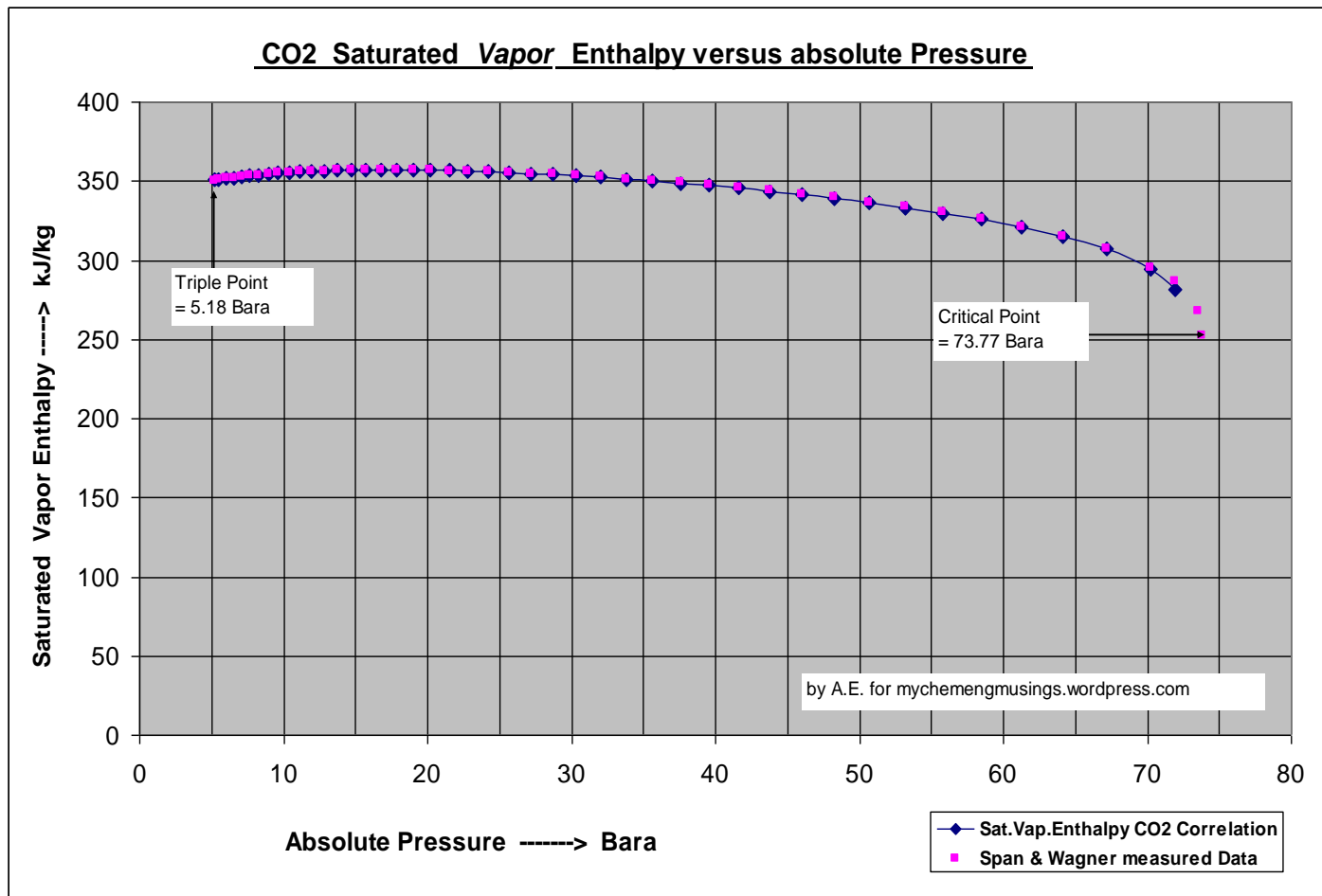
CO2 Saturated Vapor Density versus absolute Temperature



CO2 Saturated Liquid Enthalpy versus absolute Temperature







End of Post

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