Vapor Pressures from Acentric Factor Omega plus Corresponding States Principle.

Published 6 July 2019 (updated 24 Oct 2019) by A.E. for mychemengmusings.com

The vapor pressure as function of temperature can be estimated for a wide range of different, pure substances with the help of a simple equation. This post is divided in three parts, Part I, II and III.
Part I presents the equation in corresponding state format as well as an expression of the actual vapor pressure for a given substance that employs three parameters characterizing a substance: the Acentric Factor Omega plus critical pressure and critical temperature.
Part II gives numerical examples.
Part III discusses the basis for this equation.
Note that the formula's are shown in ‘excel’ style format in which multiplication is symbolized by ‘*’ and the Acentric Factor is symbolized by the capital letter ‘W’ standing for the Greek letter Omega.

Part I. The basic equation is stated in a corresponding states type formula with the reduced Pressure and Temperatures as variables and the Acentric Factor W as parameter. It reads as follows:

\[ \ln(Pr) = 5.3727 \times (1 + W) \times (1 - 1/Tr) \]  

(Eq. 1.)

In which the symbol ‘\(\ln\)’ stands for the natural logarithm; ‘\(Pr\)’ is the reduced (saturated) vapor pressure, ‘\(W\)’ is Pitzer’s Acentric Factor Omega for a particular substance and ‘\(Tr\)’ is the reduced temperature. This equation is valid for the following reduced temperature range: 0.70 = < \(Tr\) = < 1.0

The actual (saturated) vapor pressure as function of the absolute temperature can be expressed as:

\[ P = P_{crit} \times \exp(5.3727 \times (1+W) \times (1 - \frac{T_{crit}}{T})) \]  

(Eq.1a)

Discussion. The advantage of the equations is they are simple, versatile and are applicable to a very wide range of substances. The ready availability of the Acentric Factor in many thermo-physical databases [Ref 1] adds to it’s wide-ranging usefulness. The downside is that these equations, by definition, have limited validity range covering only the ‘upper’ part of the entire two phase vapor-liquid region i.e. the reduced temperature range of \(Tr = 0.7\) to 1.0 See Part III for more details.

Part II. Numerical examples.
Example (a) Propane, C3: with basic physical data: \(T_{crit} = 369.89\) Degrees Kelvin; \(P_{crit} = 42.48\) Bar abs and Acentric Factor, \(Omega = 0.157\). Data [Ref 2].
With these basic data equation 1a reads for pure Propane:
\[ P_{,nCH_3} = 42.48 \times \exp \left( 5.3727 \times (1 + 0.157) \times (1 - 369.89 / T) \right) \]

If we, for example, want to know what the vapor pressure is for a temperature of 40 degrees Celsius (absolute temperature of \( T = 313.15 \, \text{oK} \)) then calculation with the above equation 1a gives: 13.78 Bar abs, while the tabulated value is 13.69 Bar abs. (percentage error of 0.6 %)

Example (b) Water, \( \text{H}_2\text{O} \): with basic physical data: \( T_{\text{crit}} = 647.15 \, \text{Degrees Kelvin} \); \( P_{\text{crit}} = 220.64 \) Bar abs and Acentric Factor, \( \Omega = 0.3433 \). Data [Ref 2].
With these basic data the equation 1a for the vapor pressure of pure (saturated) Water reads:

\[ P_{,\text{H}_2\text{O}} = 220.64 \times \exp \left( 5.3727 \times (1+0.3433) \times (1 - 647.15 / T) \right) \]

For a temperature of 240 degrees Celsius, equal to 513.15 degrees Kelvin, the saturated steam pressure is calculated to be 33.5 Bar abs. while the tabulated value is given as 33.4 Bar abs. (Grigull).

Part III  The basis for Equation 1.
The equation in Part I is the result of bringing J.D. van der Waals’ ‘Theorem of Corresponding States’ together with K. Pitzer’s Acentric Factor.

The Theorem of Corresponding States. The original van der Waals equation of state described the relation of pressure and temperature of a single, pure substance by introducing in the universal gas law two extra terms accounting for the mutual attraction between molecules and for each molecule having a finite ‘eigen’ volume. These two terms introduced two constants ‘a’ and ‘b’ characteristic for a specific substance. It was only later that he realized that the shape of the two phase region has the critical point as its typical marking point, in other words that with respect to the critical point the two-phase behavior for all substances is the same. He was able to reformulate the original equation of state in terms of reduced temperature \( T_r \) and reduced pressure \( P_r \) in which the two constants ‘a’ and ‘b’ were eliminated. He realized that this new, reformulated, single equation is valid for all substances and gives a universal description of the liquid-vapor two-phase behavior. This became known as the ‘theorem of corresponding states’.

The theorem says that there is a fundamental ‘continuity’ of the dual liquid-vapor phase region into the single phase gas/liquid behavior where the critical point marks a continuous transition point that holds for all substances. In other words all substances show the same vapor-liquid to gas phase behavior if and only if they are compared with respect to their critical points. This theoretical discovery and insight at the time was very revealing as up to that time there were still the five so-called ‘Permanent Gasses’ that had resisted numerous attempts, notwithstanding using thousands of atmospheres of pressure, to turn each into it’s liquid phase!
The discovery of the theorem meant in practical terms that these permanent gases should be able to be liquefied but only by first cooling such gas down below their critical point and only then followed by applying pressure. The Frenchman L.P. Cailletet was the first to prove in his cryogenic laboratory this to be true by demonstrating (for the first time) the liquefaction of Oxygen.

The corresponding states theorem proved to be a unifying 'super-concept' in describing the thermo-physical properties of substances through reduced variables. However when the reduced vapor pressures of different substances are plotted against their inverse reduced temperature one would expect all the points for each substance to fall along a single line beginning in the critical point. In actual fact, however, one observes a bundle of lines appearing with each having a different slope, that have only one point in common: the critical point. See for example the following Chart in which the reduced vapor pressures of Methane, Ethane, Propane and Water are plotted against their inverse reduced temperatures. (Click on Chart to expand):

![Reduced Vapor Pressure versus inverse Reduced Temperature](chart)

**Fig. 1.** The Reduced Vapor Pressures of Methane, Ethane, Propane and Water versus the inverse Reduced Temperature.
Pitzer’s Acentric Factor Omega.
K. Pitzer introduced a new factor that uniquely characterizes a given substance in terms of its thermo-physical behavior. We will use the above Chart in which reduced vapor pressure is plotted against the inverse reduced temperature to follow his line of reasoning. He observed in the line bundle of Fig. 1 a pattern of regularity. For example in the above Chart we can see that the reduced vapor pressure lines of the first three members of the n-alkanes hydrocarbon family show progressively steeper slopes: the higher the molecular weight the steeper the slope. A similar effect is found for series of compounds with varying polarity e.g. the normal alkanols and so on. The effect of polarity per se is clearly demonstrated in Fig. 1 by the reduced vapor pressure line of Water compared to Methane both of close molecular weight (18 and 16). He noticed also that the reduced vapor pressure for the noble gases (Neon, Argon etc) all have (or happen to have) a value of 0.10 at a reduced temperature of 0.70 (note: the line of noble gases not shown in Chart here). Realizing that the noble gases all are apolar, have no polarity at all, and are of spherical shape, unlike e.g. the linear shaped normal alkanes, he turned the observations of the distinct behavior of other substances into a characteristic property by defining the deviation of the reduced vapor pressure at the reduced temperature of 0.70 from the value of Pr=0.1 into a defining characteristic factor for a given substance! Hence Pitzer’s definition of the Acentric factor omega as:

\[ \Omega = - \log_{10}(Pr) - 1 \]

with ‘Pr’ being the reduced saturated vapor pressure (Psat/Pcrit at Tr=0.7).

Omega can be interpreted as being a factor that uniquely characterizes the thermo-physical behavior of a given substance, witness the nowadays wide spread use as such in correlating physical properties. Omega can be interpreted in another way as well when we look at Fig.1 again: the factor omega is a kind of measure for the slope of a substance’s reduced vapor pressure line. It is this interpretation that we will make use of in the derivation shown below.

Derivation of Equation 1.
The Clapeyron vapor pressure relation with temperature can be written in reduced variables as:

\[ \ln(Pr) = A \times \left( \frac{1}{Tr} \right) + B \]

From the fact that this line runs through the critical point follows \( Pr=1=Tr \) and hence \( B = -A \). and thus

\[ \ln(Pr) = A \times \left( \frac{1}{Tr} - 1 \right) \]

From the definition of Omega follows the slope ‘A’ of the reduced vapor pressure line:
\[ W = - \log (Pr \text{ at } Tr=0.7) - 1 \implies \log (Pr \text{ at } Tr=0.7) = -(1+W) \] and thus:

\[ A = (\log(Pr \text{ at } Tr=1) - \log(Pr \text{ at } Tr=0.7)) / (1/0.70 - 1) = +(1+W) * 2.3333 \]

Converting from a 10 based- to natural based logarithm gives \( A = 5.3727 * (1+W) \)

Hence Equation 1: \( \ln(Pr) = 5.3727 * (1+W) * (1 - 1/Tr) \)

Note 1. It is interesting to note that a ‘unified’ plot of the reduced vapor pressures of different substances, each characterized by their Omega value, can be obtained by plotting \( 1/ (1+W) * \ln(Pr) \) against \( 1/Tr \), thus yielding one single line. All data in Fig. 1. have been re-plotted in this way and are shown in the following Chart of Fig. 2.

---

**Fig. 2.** Unified Reduced Vapor Pressure plot.

It is interesting to note in Fig.2 that at temperatures below \( Tr = 0.70 \) the individual points start to diverge more and more with temperatures approaching the triple
point. At the lower temperatures the liquid phase molecular interactions become more pronounced than is accounted for in the slope as measured by the Acentric Factor Omega!

Note 2. An equation similar to Eq. 1 maybe developed to cover the low temperature range below \( Tr = 0.70 \) by taking another known reference point, other than the critical point to determine the slope of the reduced vapor line. For example the triple point or any other known point in the vacuum range may be taken as a reference point.

References.
[Ref. 1.] An example of a database with extensive listings of Acentric Factor Omega (and other phys. properties.) is the API data base.
[Ref. 2.] For critical- and other physical data see earlier posts and refs.