2: Vapor Pressure

Distillation Science (a blend of Chemistry and Chemical Engineering)

This is Part II, Vapor Pressure of a ten-part series of technical articles on Distillation Science, as is currently practiced on an industrial level. See also Part I, Overview for introductory comments, the scope of the article series, and nomenclature.

Part II, Vapor Pressure deals with the existing pure component vapor pressure (VP) equations normally found in textbooks. The content of this article is referred to in subsequent articles. The goal of this article is to explain the limitations of these less sophisticated VP equations, to show how best to use them, and to set up the introduction of a superior VP equation form in Part IV.

The original Clausius-Clapeyron equation relating VP, temperature, vaporization molar volume change ($\Delta V_{vap}$) and latent heat of vaporization ($\Delta H_v$) dates back to mid-19th century and is derived from thermodynamic principles. The derivation is given in many college freshman-level texts and results from thermodynamic equilibrium between liquid and vapor phases. First, the differential of pressure with respect to system temperature (for both vapor and liquid) is re-arranged to:

$$\frac{dP}{dT} = \frac{\Delta H_v}{T \Delta V_{vap}} \quad \text{(2-1)}$$

If (assumption 1) the vaporization molar volume change ($\Delta V_{vap}$) is set equal to the saturated vapor volume (V) by assuming the boiling liquid’s molar volume is essentially zero; and if (assumption 2) the "Ideal Gas Law" (PV=RT) can hold for this saturated vapor, then Equation (2-1) in differential form the relationship becomes:

$$\frac{d(\ln P)}{d(1/T)} = \frac{\Delta H_{vap}}{RT} \quad \text{(2-2)}$$

When integrated, this results in the simplified Clausius-Clapeyron relationship that is found in most textbooks. However, there are limited conditions for which the above two assumptions are nearly correct: non-complex molecular structure and very low pressure (say, below atmospheric or very...
near atmospheric). For most compounds, and for most pressures encountered in normal industrial processes, neither of these assumptions holds very well and accuracy gets increasingly worse as pressure increases beyond atmospheric.

For real compounds and pressures normally encountered in industry, a term is added to the "Ideal Gas Law" (PV=RT) called compressibility, Z; so then the relationship becomes:

\[ PV = ZRT \]

Where compressibility Z is a function of that fluid’s pressure, temperature, and other physical properties such as discussed in the Part III. Note that Equation \( \text{(ref(2-3))} \) holds for both vapors and liquids: with \( Z_v \) being vapor compressibility, \( Z_L \) being liquid compressibility, and \( \Delta Z_{vap} \) being the change in compressibility with vaporization. Now Equation \( \text{(ref(2-1))} \) can be transformed into a more usable relationship for all fluids and all sub-critical pressures. In differential form, it is: \[ \frac{d\ln P}{d(1/T)} = \frac{\Delta H_{vap}}{\Delta Z_{vap}RT} \]

After integration between close temperatures \( T_1 \) and \( T_2 \) (so the ratio \( \Delta H_{vap} / \Delta Z_{vap} \) can be taken as constant over that close range), Equation \( \text{(ref(2-4))} \) becomes:

\[ \ln(P_{2}/P_{1}) = \frac{\Delta H_{vap}}{\Delta Z_{vap}R} \times (1/T_{1}-1/T_{2}) \]

It can now be understood that \( \Delta Z_{vap} \) is the measure of the net effect of removing above assumptions (1) and (2) that allowed Equation \( \text{(ref(2-2))} \). For most fluids near atmospheric pressure, \( \Delta Z_{vap} \) is about 0.95 - 0.99, but as pressures increase toward a fluid’s critical point (where vapor and liquid merge at a singularity), \( \Delta Z_{vap} \) goes to zero. (But of course, \( \Delta H_{vap} \) also goes to zero at the critical point, so the ratio \( \Delta H_{vap} / \Delta Z_{vap} \) becomes undefined at this singularity).

The evaluation of \( \Delta Z_{vap} \) normally requires use of an Equation of State (EOS), which is discussed in Part V. Using such an EOS to assess \( \Delta Z_{vap} \) would allow vapor pressure vs temperature data to exactly align with \( \Delta H_{vap} \) values. In Part IV, Equation \( \text{(ref(2-4))} \) will be further developed and integrated without use of an EOS, up to pressures close to critical (usually about 95% of critical pressure in pure component systems).

Returning back to the above integrated form of Clausius-Clapeyron, Equation \( \text{(ref(2-5))} \) suggests the commonly used empirical means to curve-fit VP data over small temperature/pressure ranges:

\[ \ln(P) = A-B/T \]

The term "B" does not have any exact scientific significance, but works as a curve-fitting parameter and is normally shown with a negative sign, so as to have a positive value. Since Equation \( \text{(ref(2-7))} \) has a limited range of application to low pressures, it can be improved for use near ambient and slightly higher pressures with empirical form for curve-fitting VP vs T, called the Antoine Equation. However the constants A, B, and C have no scientific basis either and the equation form can still only be used over modest ranges (and low pressures).

\[ \ln(P) = A-\frac{B}{T+C} \]

Additional constants D, E, F can be added to make the "extended Antoine" relationship for empirical curve-fitting; however there is still no correlation between the constants and scientific meaning.
\[ \ln(P) = A - \frac{B}{T+C} + DT + ET^2 + F \times \ln(T) \ \text{label(2-9)} \]

From an industrial distillation column design perspective, even the extended Antoine VP relationships found in handbooks are not entirely adequate: they rarely reproduce the correct VP values at $T_b$, $T_c$ and at $T_r=0.7$ (where the acentric factor is determined). That inadequacy undermines attempts to use modern Equations of State (EOS are discussed in Part V), forcing the use of the antiquated Van der Waals EOS. With any EOS, the extended Antoine VP relationship cannot connect latent heats and saturated (vapor and liquid) phase densities to vapor pressure. Additionally, none of these empirical VP equations reproduces the inflection point required by thermodynamics of a real fluid's VP vs T plot, normally occurring between $T_r=0.7$ and $T_r=0.85$. For economic reasons, many industrial processes operate at these higher pressures, so using empirical VP equations can lead to poor distillation column design. This is especially true in modern industrial applications where complex computer programs have automated several aspects of distillation column design.

In designing such an industrial-level distillation column, the various process simulation packages (e.g., ASPEN, VMG, etc) would then be fed with rather poor VP estimations. It is not uncommon with such simulation software to become non-convergent or to have the problem solution get stuck on a singularity. In the vernacular of the early days of computing, “Garbage in – Garbage out”.

The solution to this quandary is to find a better VP equation form that possesses all the criteria lacking in the VP equations shown in this article. A solution to that is proposed in Part IV.

However, Equation (ref{2-7}) and Equation (ref{2-8}) are not without merit, as long as they are used for the purpose they were derived: only for narrow ranges of temperature and at moderate pressures. Equation (ref{2-8}) (Antoine) is especially useful in correlating data taken around the atmospheric boiling point, $T_b$, to get a more accurate value from several experimental data points, rather than just one. It also allows data from several sources to be inter-compared, as long as they had a similar temperature range.

While evaluating the “A, B, and C” of Equation (ref{2-8}) may seem daunting, the solution is readily managed using some algebraic manipulation and a spreadsheet multiple regression function (e.g., MS Excel). Equation (ref{2-8}) is rewritten as the algebraically equivalent

\[ \ln(P) = A + \frac{AC-B}{T} - C \times \ln(P)/T \ \text{label(2-10)} \]

Then VP vs T data (always as absolute pressure and temperature) are converted into three columns for each data set: the dependent variable is “Ln(P)”, and the two independent variables are “1/T” and “Ln(P)/T”. When the regression is run, the regression’s intercept will equal Equation (ref{2-8})’s “A”; and the second independent variable’s coefficient (i.e., for Ln(P)/T ) will equal the negative of Equation (ref{2-8})’s “C”. The value of Equation (ref{2-8})’s “B” is determined algebraically from the first independent variable’s coefficient (i.e., for 1/T)= (AC-B). See an example of using this solution procedure in below Table 2-1.

This curve-fit parameter solution technique does not work with Equation (ref{2-9}), so often the “Extended Antoine” equation is stated differently as

\[ \ln(P) = A - \frac{B}{T+C} + DT + ET^2 \ \text{label(2-11)} \]
requiring a multiple linear regression (such as with MS Excel) be done with the four "independent" variables: 1/T, Ln(T), T, and T². Assuming the temperature range is narrow, the curve-fit quality is almost always statistically better with Equation (ref{2-8}) than with Equation (ref{2-11}), since there are two fewer constants. If the range is broader, such as spanning from atmospheric to the half-way point of critical pressure, then Equation (ref{2-11}) will give the better curve-fit.

When using experimental data to determine the normal boiling point (Tₜ), Equation (ref{2-8}) seems to work best. When using experimental data to determine the VP at T= 0.7 (i.e., evaluating the acentric factor), or inter-comparing VP measurements over a similar broader range, Equation (ref{2-11}) is preferred. Equation (ref{2-9}) is rarely used for design or data comparison, and is just mentioned for historical purposes.

Example:

PCl₃ is an important impurity to remove in producing high quality polysilicon for use in solar arrays and electronic integrated circuits (like computer chips). Part of the purification process involves distillation, and so it is desirable to know the NBP of this compound with high confidence. Researching the NIST database shows an Antoine expression (Equation (ref{2-8})), but the constants given are recalculated from a 1947 paper by Dan Stull published in I&EC. In making that paper's VP tables, he took data from several early-to-mid 20th century sources and plotted them on a Cox Chart (a graphical approximation method from the 1920's), then read "best fit" values from the Cox Chart at selected pressures. So this data source is questionable, with a possibility of data being "overly massaged". However from DeChema and Infotherm online global databases, experimental data is available from four more recent sources, with some mild disagreement in the pressure range of 1.0 atmospheres = 760 Torr = 101.325 kPa. It is decided to download the original data and develop an Antoine curve-fit, to best determine a most-likely NBP for PCl₃.

Table 2-1 shows the experimental data, sorted by temperature. DeChema and Infotherm report vapor pressures in kPa, so that pressure unit is used in the below calculation. To each data point row, columns for "1/T" and "Ln(P)/T" are added. The last two columns show the VP predicted by the Antoine regression and the difference between data point and predicted VP. Under the tabulated data, the results of the regression are shown, as well as the calculation of Antoine constants A, B, and C. And finally the best value for PCl₃'s NBP based on data along with an assessment of accuracy.

<table>
<thead>
<tr>
<th>T, K</th>
<th>VP, kPa</th>
<th>Ln(VP), dependent variable</th>
<th>1/T, independent variable</th>
<th>Ln(VP)/T, independent variable 2</th>
<th>Antoine predicted VP, kPa</th>
<th>Prediction Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>361.85</td>
<td>151.988</td>
<td>5.024</td>
<td>2.7636E-03</td>
<td>1.3884E-02</td>
<td>150.362</td>
<td>1.626</td>
</tr>
<tr>
<td>361.75</td>
<td>151.988</td>
<td>5.024</td>
<td>2.7643E-03</td>
<td>1.3887E-02</td>
<td>149.964</td>
<td>2.024</td>
</tr>
<tr>
<td>358.55</td>
<td>136.389</td>
<td>4.916</td>
<td>2.7890E-03</td>
<td>1.3709E-02</td>
<td>137.544</td>
<td>-1.155</td>
</tr>
</tbody>
</table>

https://eng.libretexts.org/Bookshelves/Chemical_Engineering/Book%3A_Distillation_Science_(Coleman)/02%3A_Vapor_Pres…

Updated: Sat, 16 Nov 2019 08:30:53 GMT
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The regression results using MS Excel's data analysis function show an $R^2 = 0.9971$ with 14 data points

**Intercept = 9.7954; Variable 1 coefficient = -2640.04; Variable 2 coefficient = 181.437**

Calculate Antoine "A", "B", and "C" per the above procedure:

Intercept = 9.7954 = Antoine "A"

Variable 1 coeff. = -2640.04 so (- Intercept x Variable 2 coeff. - Variable 1 coeff. ) = Antoine "B" = 862.795

Variable 2 coeff. = 181.437 = -1 x Antoine "C", so Antoine "C" = -181.437

The Antoine Equation for $\text{PCl}_3$ is determined as $\ln(P) = 9.7954 - \frac{862.795}{T-181.437}$

Solving Equation (ref[2-12]) for the atmospheric pressure of 101.325 kPa gives a $T_b$ of 348.09°K = 74.94°C ⇒ 74.9°C.

The average absolute difference of (data -predicted) VP = the table's last column is 0.756 kPa

Note that if the NIST webbook values were used for "A", "B" and "C", a value of 348.34°K ⇒ 75.2°C would result. In this case, the NIST listed results were pretty close the experimental values' regression. Also note that a quick search on Wikipedia's website would have offered a $T_b$ value of 76.1°C, or about a degree higher than actual results. But now that...
the best value of $T_b$ is known, and there can also be a reasonable evaluation of value's accuracy based on the regression's average error. A 0.756 kPa error at 101.325 kPa pressure equates to a change in calculated $T_b$ of 0.24°K, so the scientific answer to the question is $74.9 \pm 0.2°C$. 