

**Study of the Effects of Noisy Data on the Determination of the Enthalpy
of Vaporization from a Vapor Pressure Equation**

by

Thomas Bryan Casserly

Submitted to the
Office of Honors Programs and Academic Scholarships
Texas A&M University
in partial fulfillment of the requirements for


1998-99 University Undergraduate Research Fellows Program

April 15, 1999

Approved as to style and content by:



Dr. Kenneth R. Hall
Department of Chemical Engineering



Susanna Finnell, Executive Director
Honors Programs and Academic Scholarships

Fellows Group: Chemistry

Table of Contents

Table of Contents	ii
List of Tables	iii
List of Figures	iii
Abstract	iv
Introduction.....	1
<i>Enthalpy of Vaporization</i>	1
<i>Vapor Pressure Equations</i>	2
Approach.....	6
Results.....	6
<i>Antoine Equation</i>	6
<i>Keyes Equation</i>	7
<i>Wagner Equation</i>	8
<i>Asymptotic Equation</i>	8
Real Data Examples.....	9
Discussion	12
Literature Cited	14
Appendix A: <i>Proof of Positive Derivative for Asymptotic Equation</i>	15
Appendix B: <i>Spreadsheet Calculations and Charts</i>	22
Appendix C: <i>SAS Code and Output</i>	37
Appendix D: <i>Maple Worksheets</i>	40

List of Tables

Table 1. Noisy Vapor Pressure Data	10
--	----

List of Figures

Figure 1. Wagner Equation Fit for Methanol.....	10
Figure 2. Antoine Equation Fit for Methanol.....	11
Figure 3. Keyes Equation Fit for Methanol.....	11
Figure 4. Asymptotic Equation Fit for Methanol	12

Abstract

Chemical engineers use software tools everyday to aid them in solving complex problems. Software packages simulate virtually every aspect of a chemical process, including the use of source vapor pressure data to fit empirical constants of a vapor pressure equation. The slope of the vapor pressure is used in the calculation of the enthalpy of vaporization. Some multi-parameter vapor pressure equations are sensitive to noisy data causing errors in the expression for the relationship between temperature and vapor pressure. These errors propagate through the calculation of the enthalpy of vaporization and any design equation in which the enthalpy of vaporization appears. The enthalpy of vaporization is important in the design of multiphase reactors, heat exchangers, distillation columns and numerous other unit operations. Errors in its computation can lead to compounding errors, which gone unchecked, can lead to the construction of a chemical plant doomed to explode or otherwise fail.

To avoid the errors sometimes introduced by multi-constant vapor pressure equations a vapor pressure equation restricted to yield results that more closely mirror natural phenomena should be used. The Asymptotic equation studied is an example of a naturally constrained and very accurate vapor pressure equation.

Introduction

Chemical engineers use mathematical tools everyday to aid them in solving complex problems. Numerous software packages exist that simulate virtually every aspect of a chemical process. These simulators rely upon the information given to them and are constrained only by the programmer's wit. Vapor pressure is one type of data often used in simulators. These data are fit to an empirical expression for use in many design equations. The enthalpy of vaporization is an important quantity calculated based upon the empirical vapor pressure equation. Some multi-parameter vapor pressure equations are sensitive to noisy data causing errors in the calculation of the enthalpy of vaporization. The enthalpy of vaporization is important in the design of multiphase reactors, heat exchangers, distillation columns and numerous other unit operations. Errors in its computation can lead to compounding errors, which gone unchecked, can lead to the construction of a chemical plant doomed to explode or fail to operate.

Enthalpy of Vaporization

The enthalpy of vaporization is the amount of energy required for a species to change phase from a liquid to a vapor. The enthalpy of vaporization for a pure component is a function of temperature only and is calculated using the Clapeyron equation¹ given by

$$\Delta H = T \cdot \Delta V \cdot \frac{dP^{\text{sat}}}{dT} \quad (1)$$

where at temperature T ,

ΔH = enthalpy of vaporization

ΔV = volume change accompanying phase change

P^{sat} = vapor pressure

The enthalpy of vaporization is always a positive number, meaning that energy is needed to vaporize a liquid. The vapor phase of a pure substance is less dense than the liquid phase which signifies the volume change accompanying a phase change is always positive. This coupled with the fact that absolute temperature is non-negative, requires that the slope of the vapor pressure curve characterized by the dP^{sat}/dT term in Equation 1 must also always be positive.

Equation 1 shows the importance of an accurate expression to predict the vapor pressure of a substance as a function of temperature. Many different approaches exist for this problem which result in various forms of vapor pressure equations. Several examples of expressions to estimate vapor pressure have been studied to show the limitations and errors that can be introduced by each.

Vapor Pressure Equations

The Clapeyron equation, given in Equation 1, is an exact thermodynamic relationship. However, no thermodynamic expression gives the relationship between

vapor pressure and temperature. Therefore, any relationship between vapor pressure and temperature is empirical in nature.

Typically, the plot of the natural log of the vapor pressure *versus* the inverse of the temperature yields a reasonably straight line and serves as the starting point for many vapor pressure equations¹. The Antoine equation is an example of a vapor pressure equation based upon this observed relationship. The Antoine equation contains three adjustable parameters

$$\ln P^{\text{sat}} = A - \frac{B}{t + C} \quad (2)$$

where A , B , and C are the adjustable parameters and the temperature, t , is given in degrees Celsius.

Some vapor pressure equations are based upon the Clapeyron equation which relates ΔH to the change in temperature. If ΔH changes according to a cubic relationship such as the equation given in Equation 3, then this expression for ΔH can be substituted into a manipulated form of the Clapeyron equation.

$$\Delta H = \Delta H^{\circ} + \alpha \cdot T + \frac{1}{2}\beta \cdot T^2 + \frac{1}{3}\gamma \cdot T^3 \quad (3)$$

When the volume change accompanying the phase change is approximated by the ideal gas equation, it can then be substituted into the Clapeyron equation yielding Equation 4, while Equation 5 is the integrated form of Equation 4.

$$d \ln P^{\text{sat}} = \frac{1}{R} \left(\frac{\Delta H^{\circ}}{T^2} + \frac{\alpha}{T} + \frac{\beta}{2} + \frac{\gamma T}{3} \right) dT \quad (4)$$

$$\ln P^{\text{sat}} = \frac{1}{R} \left(-\frac{\Delta H^{\circ}}{T} + \alpha \ln T + \frac{\beta}{2} T + \frac{\gamma T^2}{6} \right) + I \quad (5)$$

Equation 5 is translated into an empirical equation of the form

$$\log P^{\text{sat}} = -\frac{A}{T} + B \log T + CT + DT^2 + E \quad (6)$$

Keyes² dropped the $B \log T$ term from the above equation to give a vapor pressure equation similar in form to the heat capacity of a substance. The Keyes four parameter vapor pressure equation is:

$$\log P^{\text{sat}} = -\frac{A}{T} + CT + DT^2 + E \quad (7)$$

Other vapor pressure equations have had different origins. The Wagner equation¹ is an excellent example of a complex vapor pressure equation usually valid over a large temperature range. The Wagner equation gives reduced vapor pressure as a function of reduced temperature, T_r :

$$\ln P_r^{\text{sat}} = \frac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{1 - \tau} \quad (8)$$

$$\tau \equiv 1 - T_r$$

$$T_r = \frac{T}{T_c}$$

The increased number of adjustable parameters in the Keyes and Wagner equations allow an accurate fit of the vapor pressure data over a wider range of temperatures.

An unusual approach to characterizing the relationship between vapor pressure and temperature is shown in *A Vapor Pressure Equation from Extended Asymptotic Behavior*³. The characteristic shape of the vapor pressure curve as it approaches the triple

point and critical point is used to fit the vapor pressure data to two functions describing the behavior in each region. These functions are then combined with an empirical constant to create one continuous vapor pressure equation from the triple point to the critical point. The final form is given in terms of dimensionless temperature and pressure in Equations 9-11.

$$p(t) = \left[p_0(t)^N + p_\infty(t)^N \right]^{1/N} \quad (9)$$

$$p_0(t) = a_0 + a_1(a_3t + 1)^{b_1/R} \exp\left(\frac{-a_2 + \frac{b_0}{R}}{a_3t + 1}\right) \quad (10)$$

$$p_\infty(t) = 2 - a_4(1-t) + a_5(1-t)^{2-\Theta} + a_6(1-t)^3 + a_7(1-t)^4 \quad (11)$$

where

$$p(t) = 1 + \frac{P - P_t}{P_c - P_t}$$

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

$p_0(t)$ = asymptotic behavior of the vapor pressure curve near the triple point

$p_\infty(t)$ = asymptotic behavior of the vapor pressure curve near the critical point

N = empirical constant

Because a_0 , a_1 , a_2 , a_3 , a_5 , a_6 , a_7 , Θ , and N are easily defined as functions of other parameters and/or the critical and triple point temperatures and pressures, the asymptotic equation reduces to contain only three adjustable parameters, b_0 , b_1 , and a_4 .

Approach

To determine the reliability of each vapor pressure equation studied, the derivative with respect to temperature was determined for each equation. The first derivative of the vapor pressure equation with respect to temperature is also the slope of the vapor pressure curve and must be positive for all temperatures between the triple point and critical point. Therefore, each vapor pressure equation was studied to determine if it is constrained against having negative values for the slope which would lead to a negative enthalpy of vaporization. Maple™ V R4 was used to evaluate the derivatives of the vapor pressure equations studied.

Results

Antoine Equation

The derivative of the Antoine equation with respect to temperature is

$$\frac{dP^{sat}}{dT} = \frac{B}{(T+C)^2} \cdot \exp\left(A - \frac{B}{T+C}\right) \quad (12)$$

Because the exponential term is always positive, and any number or quantity squared is a positive number as well, the determining factor for the slope of Antoine equation is the Antoine coefficient B . For the slope to be negative or zero, B must be less than or equal to zero. For the Antoine coefficient B to be equal to zero, the vapor pressure must be constant over the entire range of temperatures given. This is not possible even for bad data except over differential temperature ranges. For the Antoine coefficient B to be negative, the vapor pressure must decrease as temperature increases over the entire range of data. Such a phenomenon is not possible. Physically, that would mean that as a liquid

gets hotter and hotter, less and less liquid is vaporizing. Therefore, the Antoine equation generally yields positive slopes and positive enthalpies of vaporization. An exception could occur if the Antoine equation were fit to poor data collected over a very small temperature range (less than 10°C).

Keyes Equation

The derivative of the Keyes equation as determined by Maple™ is

$$\frac{dP^{\text{sat}}}{dT} = 10^{\left(\frac{-A}{T} + CT + DT^2 + E\right)} \cdot \left(\frac{A}{T^2} + C + 2DT\right) \cdot \ln(10) \quad (13)$$

Because ten raised to any power is a positive number, as is the natural log of ten, the polynomial term must also be positive. Because no constraints exist when fitting parameters A , C , D , and E , the possibility exists for the polynomial term to be less than or equal to zero. By visual inspection, it can be noted that if one or more of the constants is negative, the polynomial can be negative. Setting the polynomial term equal to zero and solving for temperature, Maple™ gives three roots, two of which are complex. The one real root is given in Equations 14 and 15 and is the temperature at which the slope of the vapor pressure curve is equal to zero.

$$T = \frac{1}{6} \cdot \frac{\text{expr}^{1/3}}{D} + \frac{1}{6} \cdot \frac{C^2}{D \cdot \text{expr}^{1/3}} - \frac{1}{6} \cdot \frac{C}{D} \quad (14)$$

$$\text{expr} = -54AD^2 - C^3 + 6D\sqrt{3A \cdot (27AD^2 + C^3)} \quad (15)$$

The Keyes equation by virtue of its additional parameters tends to fit anomalies in data that the Antoine equation cannot and, thus, is more susceptible to having a negative slope.

Wagner Equation

The derivative of the Wagner equation with respect to τ is given in Equation 16, and the relationship between that derivative and dP^{sat}/dT is given in Equation 17.

$$\frac{dP_r^{sat}}{dT} = \left(\frac{A + 1.5B\sqrt{\tau} + 3C\tau^2 + 6D\tau^5}{1-\tau} + \frac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{(1-\tau)^2} \right) \exp\left(\frac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{1-\tau} \right) \quad (16)$$

$$\frac{dP^{sat}}{dT} = - \frac{dP_r^{sat}}{d\tau} \cdot \frac{P_c}{T_c} \quad (17)$$

Again for the Wagner equation, the exponential term is always positive, which means that the polynomial term must be negative to ensure a positive slope. The negative polynomial multiplied by the negative scalar $-P_c/T_c$ gives a positive number to keep dP^{sat}/dT always positive. The polynomial simplifies to Equation 18 when ignoring multipliers that are always positive.

$$0 \geq A + 1.5B\sqrt{\tau} - 0.5B\tau^{1.5} + 3C\tau^2 - 2C\tau^3 + 6D\tau^5 - 5D\tau^6 \quad (18)$$

This equation has very complex roots which can only be solved numerically. Because no constraints exist for A , B , C , or D , it is possible to obtain negative values of dP^{sat}/dT , and subsequently negative values of ΔH .

Asymptotic Equation

The derivative of the asymptotic equation is very complex. To prove that the derivative is always positive except at the critical point, each term in the derivative was examined separately. Please refer to Appendix A for a thorough proof. In the theoretical development of the Asymptotic equation, two separate functions are combined to yield one vapor pressure equation³. These functions are an empirical characterization of the

vapor pressure of a pure component as it approaches the triple point and critical point respectively. The Asymptotic equation, by virtue of its development, is naturally constrained against fitting anomalous data. The Asymptotic equation is similar to the Antoine equation in that there are only three fitted parameters, meaning that neither equation is given the mathematical freedom to fit noisy data. Therefore, the Asymptotic equation is able to represent natural phenomena as opposed to only fitting the data accurately.

Real Data Examples

Real data were obtained from the Thermodynamics Research Center Source Database for methanol. The data were entered into an MS Excel worksheet (Appendix B) and the parameters for the Wagner, Antoine, and Keyes equations were determined. For the Asymptotic equation, a non-linear regression tool was needed. The statistics program, SAS, was used to fit the three parameters of the Asymptotic equation using the NLIN function. The Gauss-Newton method was used to determine convergence. The data were then entered into the same workbook. The derivative of each equation was also calculated using Maple™. Over the complete range of data, all four empirical expressions fit the data well. However, when the data source was limited to some noisy data in the first 125°C, the Wagner equation gives huge errors. The Antoine, Keyes, and Asymptotic equations perform fairly well under the same conditions. The source data are listed in Table 1. The plots of the raw data *versus* the fitted empirical equations are included in Figures 1-4. It should also be noted that the fit for the Asymptotic equation and the Antoine equation

using only low temperature data extrapolate to high temperatures with less than forty percent error.

Table I. Noisy Vapor Pressure Data⁴

Temp (K)	P (kPa)
175.04	0.00016
258.54	1.48654
285.35	7.2634
290.42	11.2471
291.15	10.8417
292.75	11.3324
294.56	14.0335
294.95	12.679
298.15	17.0226
298.2	15.2
301.37	20.0522
301.65	18.2652

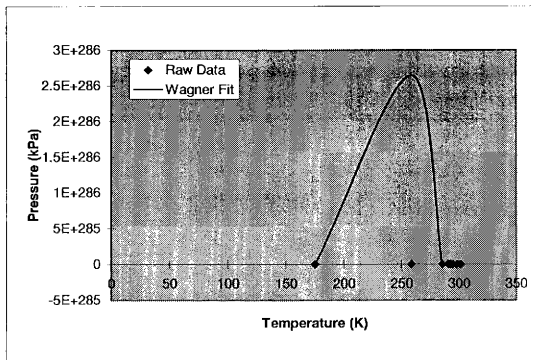


Figure 1. Wagner Equation Fit for Methanol

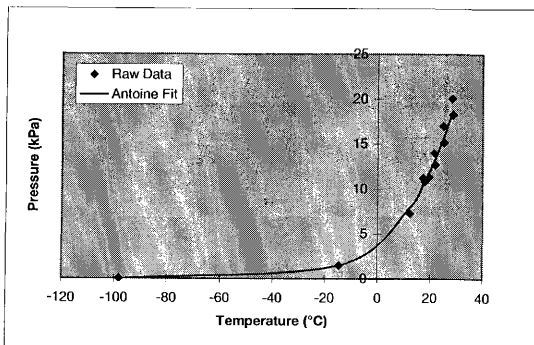


Figure 2. Antoine Equation Fit for Methanol

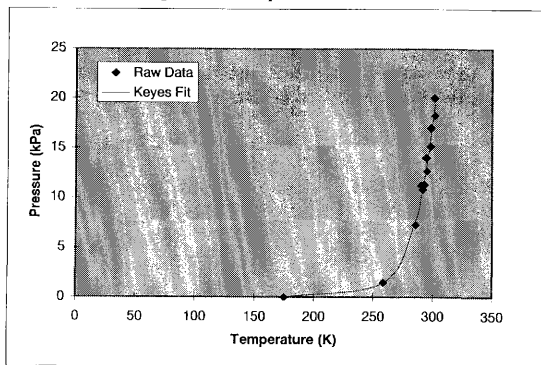


Figure 3. Keyes Equation Fit for Methanol

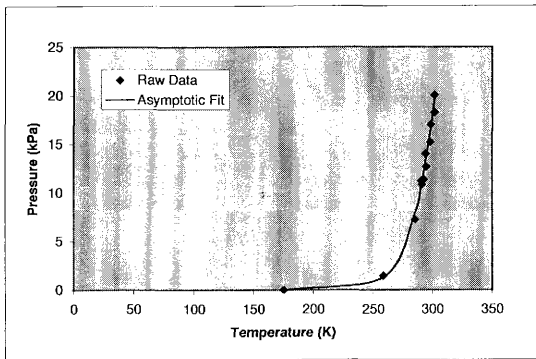


Figure 4. Asymptotic Equation Fit for Methanol

Discussion

Noisy data analyzed using multi-constant empirical equations have the potential to cause great errors in the representation of vapor pressure as a function of temperature. These errors propagate further when this expression for vapor pressure is used to calculate quantities such as the enthalpy of vaporization which have a large impact in the design of chemical reactors, distillation columns, heat exchangers and other unit operations. To avoid errors that can be overlooked by software users, the applications must be improved. Because the Wagner and Keyes equations have four empirical constants, the equations have the mathematical flexibility to fit data very accurately. This seemingly positive aspect becomes very negative and even sometimes dangerous when the equations are fit to noisy data. By virtue of the same four parameters that allow the Wagner and Keyes equations to fit data accurately, the equations can fit noisy data yielding physically impossible

relationships between vapor pressure and temperature. This ability to fit noisy data is a characteristic of nearly all vapor equations with more than three constants. This misrepresentation of the relationship between vapor pressure and temperature can have disastrous effects on the design reactors and other unit operations.

To avoid the problems that can plague multi-constant vapor pressure equations, the use a vapor pressure equation that is restricted to yield results that more closely mirror natural phenomena is suggested. The Asymptotic equation studied gives very accurate vapor pressure data over the entire range of temperatures from triple point to critical point and is an excellent example of constrained vapor pressure equation.

Literature Cited

1. Smith, J.M., Van Ness, H.C., Abbott, M.M. Introduction to Chemical Engineering Thermodynamics. Fifth Edition, McGraw-Hill: New York, 1996. pp. 126-128, 196-199.
2. Steiner, Luke E. Introduction to Chemical Thermodynamics. Second Edition, McGraw-Hill: New York, 1948. pp. 198-207.
3. Eubank, P.T., Hall, K.R., Holste, J.C., Iglesias-Silva, G.A., Marsh, K.N., "A Vapor Pressure Equation from Extended Asymptotic Behavior." *AIChE Journal*, September 1987, Vol.33, No. 9: pp. 1550-1556.
4. Thermodynamics Research Center Databases for Chemistry and Engineering, TRC SOURCE Database Version 1998-2. Texas Engineering Experiment Station, Texas A&M University, 1998.

Appendix A:

Proof of Positive Derivative for Asymptotic Equation

1.

Appendix A - Proof of Asymptotic Equation's derivative being always positive
 Asymptotic E.O.S.

> restart:with(linalg):

Warning, new definition for norm

Warning, new definition for trace

> Asymptotic:= [p[0] (t)^N+p[infinity] (t)^N]^(1/N);

$$\text{Asymptotic} := [p_0(t)^N + p_\infty(t)^N]^{\left(\frac{1}{N}\right)}$$

> p_triple:=a[0]+a[1]*(a[3]*t+1)^(b[0]/R)*exp((-a[2]+b[0]/R)/(a[3]*t+1));

$$p_triple := a_0 + a_1 (a_3 t + 1) e^{\left(\frac{b_0}{R}\right) \left(\frac{-a_2 + \frac{b_0}{R}}{a_3 t + 1}\right)}$$

> p_infinity:=2-a[4]*(1-t)+a[5]*(1-t)^(2-Theta)+a[6]*(1-t)^3+a[7]*(1-t)^4;

$$p_infinity := 2 - a_4 (1 - t) + a_5 (1 - t)^{(2-\Theta)} + a_6 (1 - t)^3 + a_7 (1 - t)^4$$

> Hall:=(p_triple^N+p_infinity^N)^(1/N);

Hall :=

$$\left(\left(a_0 + a_1 (a_3 t + 1) \left(\frac{b_0}{R}\right) e^{\left(\frac{-a_2 + \frac{b_0}{R}}{a_3 t + 1}\right)} \right)^N + (2 - a_4 (1 - t) + a_5 (1 - t)^{(2-\Theta)} + a_6 (1 - t)^3 + a_7 (1 - t)^4)^N \right)^{\left(\frac{1}{N}\right)}$$

> Dhall:=diff(Hall, t);

$$Dhall := (%4^N + %1^N)^{\left(\frac{1}{N}\right)} \left(\frac{\%4^N N \left(\frac{a_1 \%3 b_0 a_3 \%2}{R (a_3 t - 1)} - \frac{a_1 \%3 \left(-a_2 + \frac{b_0}{R}\right) a_3 \%2}{(a_3 t + 1)^2} \right)}{\%4} \right)$$

$$+ \frac{\%1^N N \left(a_4 - \frac{a_5 (1 - t)^{(2-\Theta)} (2 - \Theta)}{1 - t} - 3 a_6 (1 - t)^2 - 4 a_7 (1 - t)^3 \right)}{\%1} \Bigg) / (N (%4^N + %1^N))$$

$$\%1 := 2 - a_4 (1 - t) + a_5 (1 - t)^{(2-\Theta)} + a_6 (1 - t)^3 + a_7 (1 - t)^4$$

$$\%2 := e^{\left(\frac{-a_2 + \frac{b_0}{R}}{a_3 t + 1} \right)}$$

$$\%3 := (a_3 t + 1)^{\left(\frac{b_0}{R} \right)}$$

$$\%4 := a_0 + a_1 \%3 \%2$$

```
> a[0]:=1-P[t]/(P[c]-P[t]);a[1]:=- (a[0]-1)*exp(a[2]-b[0]/R);a[2]:=b[1]/(R*T[t]);a[3]:=(T[c]-T[t])/T[t];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;N:=87*T[t]/T[c];Theta:=0.2;R:=8.314;
```

$$a_0 := 1 - \frac{P_t}{P_c - P_t}$$

$$a_1 := \frac{P_t e^{\left(a_2 - \frac{b_0}{R} \right)}}{P_c - P_t}$$

$$a_2 := \frac{b_1}{R T_t}$$

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

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

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

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

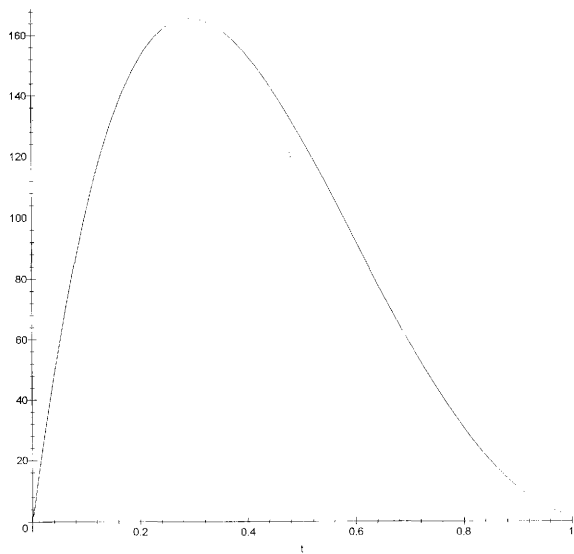
$$N := 87 \frac{T_t}{T_c}$$

$$\Theta := .2$$

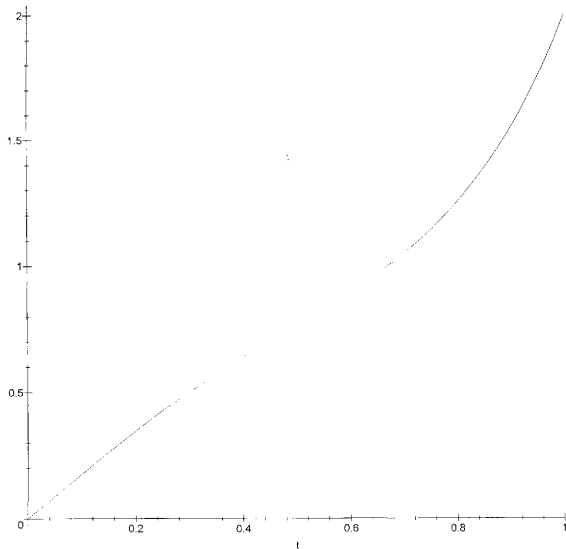
$$R := 8.314$$

```
> a[4]:=-17.457;plot(%1,t=0..1);a[4]:=5.793;plot(%1,t=0..1);
```

$$a_4 := -17.457$$



$$a_4 := 5.793$$



By inspection, $a[0]$, $a[1]$, $a[3]$, N , Θ , $\%2$, $\%3$, and thus $\%4$ are all positive, and if $b[1]$ is positive, then so is $a[2]$. If $a[4]$ is between $-17.457 < a[4] < 5.793$, then $\%1$ is always positive

```
> poly1 := (a[1]**3*b[0]*a[3]**2) / (R*(a[3]*t+1)) - (a[1]**3*(-a[2]+b[0]/
R)*a[3]**2) / (a[3]*t+1)^2;
```

$$poly1 := .1202790474 \frac{P_t e^{\left(.1202790474 \frac{b_1}{T_t} - 1202790474 b_0 \right) \%1} (-.1202790474 b_0) b_0 (T_c - T_t) e^{\left(\frac{\%2}{\%1} \right)}}{(P_c - P_t) T_t \%1}$$

$$\frac{P_t e^{\left(\frac{.1202790474 b_1}{T_i} - .1202790474 b_0 \right)} \%1^{(.1202790474 b_0)} \%2 (T_c - T_i) e^{\left(\frac{\%2}{\%1} \right)}}{(P_c - P_t) \%1^2 T_i}$$

$$\%1 := \frac{(T_c - T_i) t}{T_i} + 1$$

$$\%2 := -.1202790474 \frac{b_1}{T_i} + .1202790474 b_0$$

%1 is always positive, %2 can be assumed to be always negative because b[1] is always positive and b[0] is always negative.

That makes the first term positive from which a negative second term is subtracted which is the same as adding the absolute value of the second term yielding an always positive first poly term.

Now to check out the second.

```
> restart; Theta := 0.2; a[5] := -.11599104 + 0.29506258*a[4]^2 - 0.00021222*a[4]^5; a[6] := -.01546028 + 0.08978160*a[4]^2 - 0.05322199*a[4]^3; a[7] := 0.05725757 - 0.06817687*a[4] + 0.00047188*a[4]^5; poly2 := a[4] - a[5]*(1-t)^(2-Theta)* (2-Theta) / (1-t) - 3*a[6]*(1-t)^2 - 4*a[7]*(1-t)^3;
```

Θ := .2

$$a_5 := -.11599104 + .29506258 a_4^2 - .00021222 a_4^5$$

$$a_6 := -.01546028 + .08978160 a_4^2 - .05322199 a_4^3$$

$$a_7 := .05725757 - .06817687 a_4 + .00047188 a_4^5$$

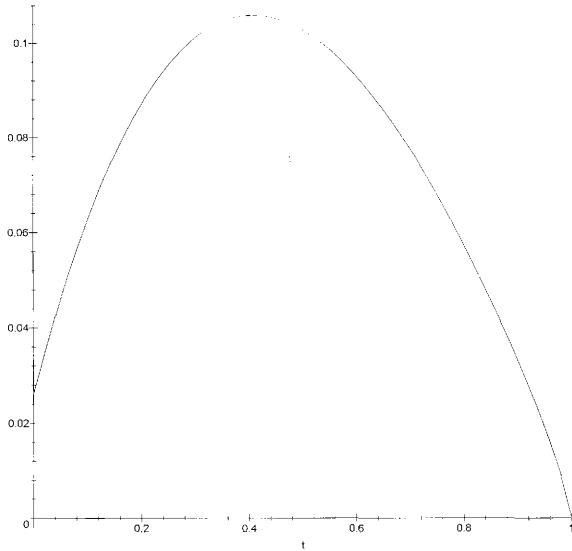
$$poly2 := a_4 - 1.8 (-.11599104 + .29506258 a_4^2 - .00021222 a_4^5) (1-t)^8$$

$$- 3 (-.01546028 + .08978160 a_4^2 - .05322199 a_4^3) (1-t)^2$$

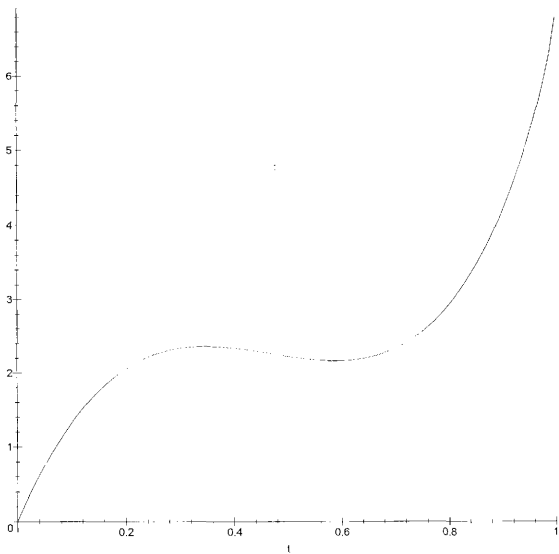
$$- 4 (.05725757 - .06817687 a_4 + .00047188 a_4^5) (1-t)^3$$

```
> a[4] := 0; plot(poly2, t=0..1); a[4] := 6.794; plot(poly2, t=0..1);
```

$$a_4 := 0$$



$$a_4 := 6.794$$



Again, this poly2 is dependant upon the value of $a[4]$, poly2 is always positive when $0 < a[4] < 6.794$

This means that if $a[4]$ is within the specified range e.g. $0 < a[4] < 5.793$, and $b[0]$ and $b[1]$ are negative and positive respectfully, then the derivative of the Asymptotic Equation is always positive for temperatures between the triple and critical points.

Appendix B:
Spreadsheet Calculations and Charts

;

Methanol Data (Wagner)

TRC DATABASES FOR CHEMISTRY AND ENGINEERING TRC SOURCE DATABASE Version 1998-2
 COPYRIGHT (C) 1991-98 TEXAS ENGINEERING EXPERIMENT STATION, TEXAS A&M

Methanol CAS No. 67-56-1 Formula CH4O MW : 32.04216

*** A. Critical constants

Property	Value	Units	Reference
P_c	8060	kPa	1988 delpoo 0
P_c	8060	kPa	1990 lydtso 0
T_c	512.5	K	1988 delpoo 0
T_c	512.5	K	1990 lydtso 0

Wagner Equation			
D	C	B	A
-1549.894312	2937.42091	-5331.6	3740.3962
2055.44488	3966.80611	7274.162	5134.4028
0.998116059	0.03812314	#N/A	#N/A
927.1538244	7	#N/A	#N/A
5.390003936	0.01017362	#N/A	#N/A

*** B. Vapor Pressure and Boiling Point

$T_c = 512.5$ K

$P_c = 8060$ kPa

Temp (K)	P (kPa)	P_r	$\ln P_r^{\text{sat}}$	$\tau = 1 - T_r$	$\tau^{1.5}$	τ^3	τ^6	$(1-\tau) \ln P_r^{\text{sat}}$	Wagner Equation		
									dP^{sat}/dT	Pcalc	Error
175.04	0.00016	1.9851E-08	-17.735006	0.658459	0.534309	0.28548632	0.0815024	-6.057239759	#NUM!	#NUM!	#NUM!
258.54	1.48654	0.00018443	-8.5982176	0.495532	0.348825	0.12167864	0.0148057	-4.337528134	-6.62E+286	2.6E+286	1.78E+286
285.35	7.2634	0.00090117	-7.0118208	0.44322	0.295072	0.08706761	0.0075808	-3.904045004	-3.43E+260	1.7E+260	2.33E+259
290.42	11.2471	0.00139542	-6.5745585	0.433327	0.285248	0.08136671	0.0066205	-3.725625921	-1.36E+256	7E+255	6.19E+254
291.15	10.8417	0.00134512	-6.611269	0.431902	0.283843	0.08056696	0.006491	-3.755845808	-3.26E+255	1.7E+255	1.54E+254
292.75	11.3324	0.001406	-6.567003	0.42878	0.280771	0.07883245	0.0062146	-3.751200225	-1.45E+254	7.5E+253	6.64E+252
294.56	14.0335	0.00174113	-6.3532215	0.425249	0.277309	0.07690051	0.0059137	-3.651521809	-4.46E+252	2.3E+252	1.67E+251
294.95	12.679	0.00157308	-6.4547218	0.424488	0.276565	0.07648841	0.0058505	-3.714771086	-2.12E+252	1.1E+252	8.79E+250
298.15	17.0226	0.00211199	-6.160127	0.418244	0.270486	0.07316255	0.0053528	-3.583691422	-5.01E+249	2.7E+249	1.58E+248
298.2	15.2	0.00188586	-6.2733734	0.418146	0.270391	0.07311137	0.0053453	-3.650185269	-4.57E+249	2.4E+249	1.61E+248
301.37	20.0522	0.00248787	-5.99633	0.411961	0.264414	0.06991466	0.0048881	-3.526076021	-1.28E+247	7E+246	3.49E+245
301.65	18.2652	0.00226615	-6.0896712	0.411415	0.263888	0.06963686	0.0048493	-3.584291366	-7.66E+246	4.2E+246	2.29E+245

Methanol Data (Wagner)

TRC DATABASES FOR CHEMISTRY AND ENGINEERING TRC SOURCE DATABASE Version 1998-2
 COPYRIGHT (C) 1991-98 TEXAS ENGINEERING EXPERIMENT STATION, TEXAS A&M

Methanol CAS No. 67-56-1 Formula CH₄O MW : 32.04216

*** A. Critical constants

Property	Value	Units	Reference
P _c	8060	kPa	1988 delpoo 0
P _c	8060	kPa	1990 lydtso 0
T _c	512.5	K	1988 delpoo 0
T _c	512.5	K	1990 lydtso 0

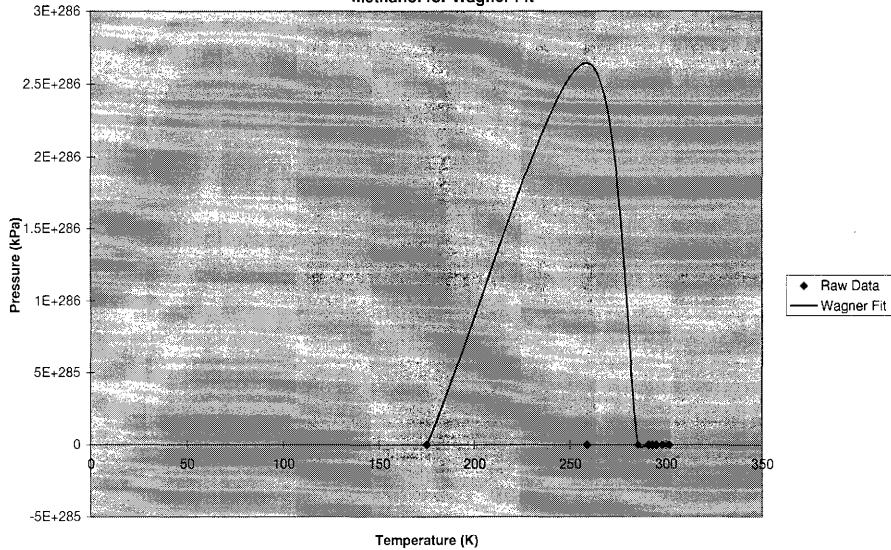
Wagner Equation				
D	C	B	A	
-1549.894312	2937.42091	-5331.6	3740.3962	
2055.44488	3966.80611	7274.162	5134.4028	
0.998116059	0.03812314	#N/A	#N/A	
927.1538244	7	#N/A	#N/A	
5.390003936	0.01017362	#N/A	#N/A	

*** B. Vapor Pressure and Boiling Point

T_b = 512.5 K
 P_c = 8060 kPa

Temp (K)	P (kPa)	P _r	ln P _r ^{sat}	τ = 1 - T _r	τ ^{1.5}	τ ³	τ ⁶	(1-τ)*ln P _r ^{sat}	Wagner Equation		
									dP ^{sat} /dT	Pcalc	Error
175.04	0.00016	1.9851E-08	-17.735006	0.65846	0.534309	0.2854863	0.0815024	-6.057239759	#NUM!	#NUM!	#NUM!
258.54	1.48654	0.00018443	-8.5982176	0.49553	0.348825	0.1216786	0.0148057	-4.337528134	-6.82E+286	2.6E+286	1.78E+286
285.35	7.2634	0.00090117	-7.0118208	0.44322	0.295072	0.0870676	0.0075808	-3.904045004	-3.43E+260	1.7E+260	2.33E+259
290.42	11.2471	0.00139542	-6.5745585	0.43333	0.285248	0.0813667	0.0066205	-3.725625921	-1.36E+256	7E+255	6.19E+254
291.15	10.8417	0.00134512	-6.611289	0.4319	0.283843	0.080567	0.006491	-3.755845808	-3.26E+255	1.7E+255	1.54E+254
292.75	11.3324	0.001406	-6.567003	0.42878	0.280771	0.0788325	0.0062146	-3.751200225	-1.45E+254	7.5E+253	6.64E+252
294.56	14.0335	0.00174113	-6.3532215	0.42525	0.277309	0.0769005	0.0059137	-3.651521809	-4.46E+252	2.3E+252	1.67E+251
294.95	12.679	0.00157308	-6.4547218	0.42449	0.276565	0.0764884	0.0058505	-3.714771086	-2.12E+252	1.1E+252	8.79E+250
298.15	17.0226	0.00211199	-6.160127	0.41824	0.270486	0.0731626	0.0053528	-3.583691422	-5.01E+249	2.7E+249	1.58E+248
298.2	15.2	0.00188586	-6.2733734	0.41815	0.270391	0.0731114	0.0053453	-3.650185269	-4.57E+249	2.4E+249	1.61E+248
301.37	20.0522	0.00248787	-5.99633	0.41196	0.264414	0.0699147	0.0048881	-3.526076021	-1.26E+247	7E+246	3.49E+245
301.65	18.2652	0.00226615	-6.0896712	0.41141	0.263888	0.0696369	0.0048493	-3.584291366	-7.66E+246	4.2E+246	2.29E+245
325.412	81.2948	0.00760481	-4.8789738	0.38505	0.220561	0.048647	0.0023565	-3.09790562	-9.2E+228	5.5E+228	9.04E+226
373.1	352.9	0.04378412	-3.1284841	0.272	0.141858	0.0201236	0.000405	-2.277536428	-5.9E+194	3.4E+194	9.65E+191
396.483	889.478	0.08554293	-2.4587369	0.22637	0.107706	0.0116007	0.0001346	-1.90214127	-1.5E+178	7.7E+175	1.11E+173
423.15	1392.05	0.17271092	-1.7561361	0.17434	0.072795	0.0052991	2.808E-05	-1.449968742	-2.03E+151	8.5E+150	6.12E+147
453.17	2702.7	0.33532258	-1.0928623	0.11577	0.039369	0.0015515	2.407E-06	-0.968109301	-1.45E+116	4.7E+115	1.74E+112
466.483	3447.38	0.42771464	-0.849293	0.08979	0.026595	0.0007239	5.24E-07	-0.773041095	-1.83E+97	5.26E+96	1.527E+93
497.594	6205.28	0.78988586	-0.281513	0.02906	0.00496	2.48E-05	0.053E-10	-0.25390694	-2.920E+41	5.9E+40	9.513E+36
498.15	6162.43	0.76458948	-0.2684424	0.028	0.004685	2.195E-05	4.819E-10	-0.25092599	-1.851E+40	3.7E+39	6.005E+35
503.15	8897.49	0.85576799	-0.155756	0.01824	0.002464	6.072E-08	3.687E-11	-0.152914382	-1.052E+29	1.95E+28	2.821E+24
503.81	8962	0.86377171	-0.1464468	0.01698	0.002208	4.875E-05	2.377E-11	-0.143963601	-2.944E+27	5.38E+26	7.734E+22
504.261	8894.76	0.85542928	-0.1581519	0.01608	0.002038	4.155E-08	1.726E-11	-0.153841541	-2.497E+26	4.53E+25	6.571E+21
505.15	6958.36	0.8633201	-0.1469697	0.01434	0.001717	2.95E-06	8.701E-12	-0.144861981	-1.818E+24	3.26E+23	4.664E+19

Methanol for Wagner Fit



Methanol Data (Antoine)

TRC DATABASES FOR CHEMISTRY AND ENGINEERING TRC SOURCE DATABASE Version 1998-2

COPYRIGHT (C) 1991-98 TEXAS ENGINEERING EXPERIMENT STATION, TEXAS A&M

Methanol CAS No. 67-56-1 Formula CH₄O MW : 32.04216

*** A. Critical constants

Property	Value	Units	Reference
P _c	8060	kPa	1988 delpoo 0
P _c	8060	kPa	1990 lydtso 0
T _c	512.5	K	1988 delpoo 0
T _c	512.5	K	1990 lydtso 0

Antoine Equation		
324.99177	16.14568001	-239.65811
19.448252	0.954453608	14.8951431
0.96951	6.857769697	#N/A
143.08938	9	#N/A
13458.703	423.2610469	#N/A

*** B. Vapor Pressure and Boiling Point

T_c = 512.5 KP_c = 8060 kPa

A	B	C
16.14568	3544.45132	239.658106

Temp (K)	T (°C)	P (kPa)	ln P ^{sat}	T/ln(P ^{sat})	1/ln(P ^{sat})	T (°C)	Antoine Equation		
							dPsat/dT	Pcalc	Error
175.04	-98.11	0.00016	-8.74034	11.22497	-0.11441	-98.11	3.947E-06	0.000137082	14.3%
258.54	-14.61	1.48654	0.396451	-36.8519	2.522378	-14.61	0.0063528	1.485765917	0.1%
285.35	12.2	7.2634	1.982848	6.152766	0.504325	12.2	0.0212798	7.944443709	9.4%
290.42	17.27	11.2471	2.42011	7.136038	0.413204	17.27	0.0258524	10.48747242	6.8%
291.15	18	10.8417	2.3834	7.552237	0.419569	18	0.0265667	10.90549741	0.6%
292.75	19.6	11.3324	2.427666	8.073599	0.411918	19.6	0.0281835	11.87177946	4.8%
294.56	21.41	14.0335	2.641447	8.105405	0.37858	21.41	0.0300991	13.05210607	7.0%
294.95	21.8	12.679	2.539947	8.582856	0.393709	21.8	0.0305242	13.31912575	5.0%
298.15	25	17.0226	2.834542	8.819767	0.352791	25	0.0341804	15.69140925	7.8%
298.2	25.05	15.2	2.721295	9.205175	0.367472	25.05	0.0342399	15.73115383	3.5%
301.37	28.22	20.0522	2.998339	9.411878	0.333518	28.22	0.0381729	18.43216598	8.1%
301.65	28.5	18.2652	2.904998	9.810679	0.344234	28.5	0.0385353	18.68859006	2.3%

Methanol Data (Antoine)

TRC DATABASES FOR CHEMISTRY AND ENGINEERING TRC SOURCE DATABASE Version 1998-2
 COPYRIGHT (C) 1991-98 TEXAS ENGINEERING EXPERIMENT STATION, TEXAS A&M

Methanol CAS No. 67-56-1 Formula CH₄O MW: 32.04216

*** A. Critical constants

Property	Value	Units	Reference
P _c	8060	kPa	1988 delpoo 0
P _c	8060	kPa	1990 lydtso 0
T _c	512.5	K	1988 delpoo 0
T _c	512.5	K	1990 lydtso 0

Antoine Equation		
324.99177	16.14568001	-239.65811
19.448252	0.954453608	14.8951431
0.96951	6.857769697	#N/A
143.08938		9 #N/A
13458.703	423.2610469	#N/A

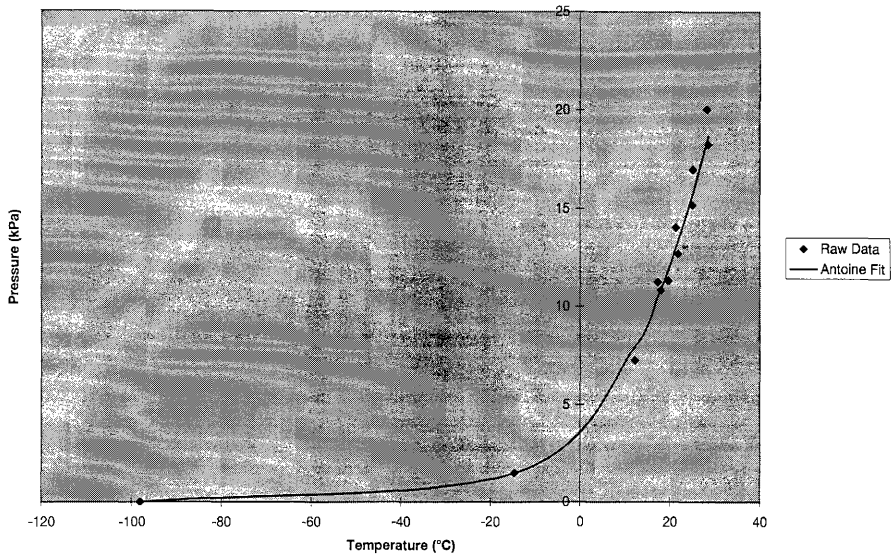
*** B. Vapor Pressure and Boiling Point

T_c = 512.5 KP_c = 8060 kPa

A	B	C
16.14568	3544.45132	239.658106

Antoine Equation									
Temp (K)	T (°C)	P (kPa)	ln P ^{sat}	T/ln(P ^{sat})	1/ln(P ^{sat})	T (°C)	dP _{sat} /dT	Pcalc	Error
175.04	-98.11	0.00016	-8.74034	11.22497	-0.11441	-98.11	3.947E-06	0.000137082	14.3%
258.54	-14.61	1.48654	0.396451	-36.8519	2.522378	-14.61	0.0063528	1.485765917	0.1%
285.35	12.2	7.2634	1.982848	6.152766	0.504325	12.2	0.0212798	7.944443709	9.4%
290.42	17.27	11.2471	2.42011	7.136038	0.413204	17.27	0.0258524	10.48747242	6.8%
291.15	18	10.8417	2.3834	7.552237	0.419569	18	0.0265667	10.90549741	0.6%
292.75	19.6	11.3324	2.427666	8.073599	0.411918	19.6	0.0281835	11.87177946	4.8%
294.56	21.41	14.0335	2.641447	8.105405	0.37858	21.41	0.0300991	13.05210607	7.0%
294.95	21.8	12.679	2.539947	8.582856	0.393709	21.8	0.0305242	13.31912575	5.0%
298.15	25	17.0226	2.834542	8.819767	0.352791	25	0.0341804	15.69140925	7.8%
298.2	25.05	15.2	2.721295	9.205175	0.367472	25.05	0.0342399	15.73115383	3.5%
301.37	28.22	20.0522	2.998339	9.411878	0.333518	28.22	0.0381729	18.43216598	8.1%
301.65	28.5	18.2652	2.904998	9.810679	0.344234	28.5	0.0385353	18.68859006	2.3%
325.412	52.262	61.2948	4.115605	12.69822	0.242972	52.262	0.0791979	54.80744092	10.6%
373.1	99.95	352.9	5.866185	17.03833	0.170469	99.95	0.2301943	301.5070277	14.6%
396.483	123.333	689.476	6.535932	18.86999	0.153	123.333	0.3398287	590.5841075	14.3%
423.15	150	1392.05	7.238533	20.72243	0.13815	150	0.4898155	1152.131517	17.2%
453.17	180.02	2702.7	7.902007	22.78156	0.12655	180.02	0.6825744	2208.430449	18.3%
466.483	193.333	3447.38	8.14537	23.73533	0.122769	193.333	0.7733548	2863.248363	16.9%
497.594	224.444	6205.28	8.733156	25.70022	0.114506	224.444	0.9907168	4956.508887	20.1%
498.15	225	6162.43	8.726225	25.78434	0.114597	225	0.9946122	5002.011733	18.8%
503.15	230	6897.49	8.836913	26.0213	0.113136	230	1.0295922	5425.169199	21.3%
503.81	230.66	6962	8.848222	26.06851	0.113017	230.66	1.0342013	5482.930167	21.2%
504.261	231.111	8894.76	8.838517	26.14816	0.113141	231.111	1.0373495	5522.659139	19.9%
505.15	232	6958.36	8.847699	26.22151	0.113024	232	1.0435519	5601.590385	19.5%

Methanol for Antoine Fit



Methanol Data (Keyes)

TRC DATABASES FOR CHEMISTRY AND ENGINEERING TRC SOURCE DATABASE Version 1998-2
 COPYRIGHT (C) 1991-98 TEXAS ENGINEERING EXPERIMENT STATION, TEXAS A&M

Methanol CAS No. 67-56-1 Formula CH₄O MW : 32.04216

*** A. Critical constants

Property	Value	Units	Reference
P _c	8060	kPa	1988 delpoo 0
P _c	8060	kPa	1990 lydtso 0
T _c	512.5	K	1988 delpoo 0
T _c	512.5	K	1990 lydtso 0

Keyes Equation			
D	C	A	E
0.0001381	-0.105397	4208.840376	34.4655835
0.0001472	0.108513	2032.863573	26.0960718
0.9997195	0.0280118	#N/A	#N/A
9504.8327	8	#N/A	#N/A
22.37421	0.0062773	#N/A	#N/A

*** B. Vapor Pressure and Boiling Point

T_c = 512.5 K

P_c = 8060 kPa

Temp (K)	P (kPa)	-1/T	T	T ²	Log(P ^{sat})	Keyes Equation		
						dP _{sat} /dT	P _{calc}	Error
175.04	0.00016	-0.005713	175.04	30639	-3.79588	2.96E-05	0.00016	0.0%
258.54	1.48654	-0.0038679	258.54	66842.93	0.172177	0.098796	1.4798074	0.5%
285.35	7.2634	-0.0035045	285.35	81424.62	0.86114	0.4472577	7.7309345	6.4%
290.42	11.2471	-0.0034433	290.42	84343.78	1.051041	0.5890516	10.341715	8.0%
291.15	10.8417	-0.0034347	291.15	84768.32	1.035097	0.612838	10.780347	0.6%
292.75	11.3324	-0.0034159	292.75	85702.56	1.054322	0.6683716	11.804675	4.2%
294.56	14.0335	-0.0033949	294.56	86765.59	1.147166	0.7372797	13.075768	6.8%
294.95	12.679	-0.0033904	294.95	86995.5	1.103085	0.7530357	13.366369	5.4%
298.15	17.0226	-0.003354	298.15	88893.42	1.231026	0.8958039	15.997854	6.0%
298.2	15.2	-0.0033535	298.2	88923.24	1.181844	0.8982392	16.042705	5.5%
301.37	20.0522	-0.0033182	301.37	90823.88	1.302162	1.0671633	19.150069	4.5%
301.65	18.2652	-0.0033151	301.65	90992.72	1.261624	1.0835554	19.451164	6.5%

Methanol Data (Keyes)

TRC DATABASES FOR CHEMISTRY AND ENGINEERING TRC SOURCE DATABASE Version 1998-2
 COPYRIGHT (C) 1991-98 TEXAS ENGINEERING EXPERIMENT STATION, TEXAS A&M

Methanol CAS No. Formula MW : 32.04216
 67-56-1 CH4O

*** A. Critical constants

Property	Value	Units	Reference
P_c	8060	kPa	1988 delpool 0
P_c	8060	kPa	1990 lydtso 0
T_c	512.5	K	1988 delpool 0
T_c	512.5	K	1990 lydtso 0

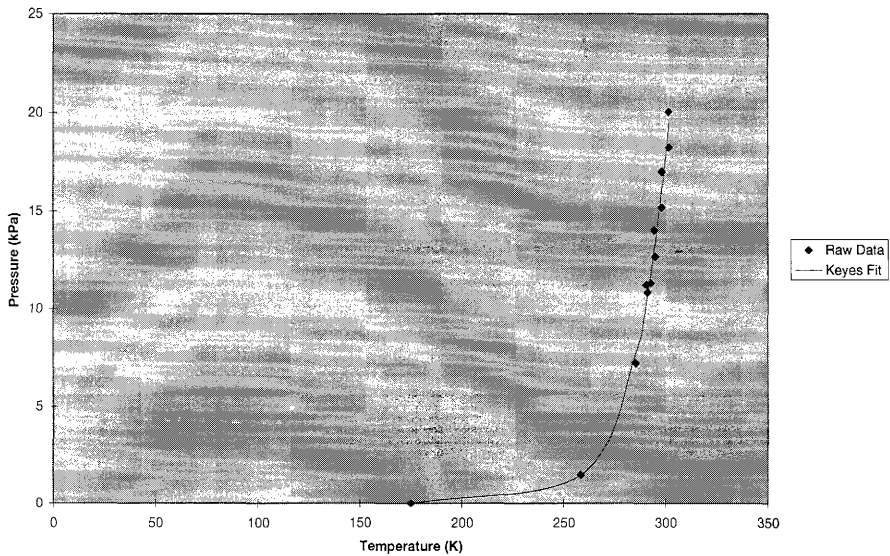
Keyes Equation			
D	C	A	E
0.0001381	-0.105397	4208.840376	34.4655835
0.0001472	0.108513	2032.863573	26.0960718
0.9997195	0.0280118	#N/A	#N/A
9504.8327	8	#N/A	#N/A
22.37421	0.0062773	#N/A	#N/A

*** B. Vapor Pressure and Boiling Point

 $T_c = 512.5$ K $P_c = 8060$ kPa

Temp (K)	P (kPa)	-1/T	T	T ²	Log(P ^{sat})	Keyes Equation		
						dPsat/dT	Pcalc	Error
175.04	0.00016	-0.005713	175.04	30639	-3.79588	2.96E-05	0.00016	0.0%
258.54	1.48654	-0.0038679	258.54	66842.9	0.172177	0.098796	1.4798074	0.5%
285.35	7.2634	-0.0035045	285.35	81424.8	0.86114	0.4472577	7.7309345	6.4%
290.42	11.2471	-0.0034433	290.42	84343.8	1.051041	0.5890516	10.341715	8.0%
291.15	10.8417	-0.0034347	291.15	84768.3	1.035097	0.612838	10.780347	0.6%
292.75	11.3324	-0.0034159	292.75	85702.6	1.054322	0.6683716	11.804675	4.2%
294.56	14.0335	-0.0033949	294.56	86765.6	1.147166	0.7372797	13.075768	6.8%
294.95	12.679	-0.0033904	294.95	86995.5	1.103085	0.7530357	13.386369	5.4%
298.15	17.0226	-0.003354	298.15	88893.4	1.231026	0.8958039	15.997854	6.0%
298.2	15.2	-0.0033535	298.2	88923.2	1.181844	0.8982392	16.042705	5.5%
301.37	20.0522	-0.0033182	301.37	90823.9	1.302162	1.0671633	19.150069	4.5%
301.65	18.2652	-0.0033151	301.65	90992.7	1.261624	1.0835554	19.451164	6.5%
325.412	61.2948	-0.003073	325.412	105893	1.787424	4.0594434	72.703559	18.6%
373.1	352.9	-0.0026802	373.1	139204	2.547652	79.036645	1229.7417	248.5%
396.483	689.476	-0.0025222	396.483	157199	2.838519	425.26023	5974.7872	766.6%
423.15	1392.05	-0.0023632	423.15	179056	3.143655	2633.0918	45067.886	3137.5%
453.17	2702.7	-0.0022067	453.17	205393	3.431798	56240.594	608192.36	22329.1%
466.483	3447.38	-0.0021437	466.483	217606	3.537489	213576.59	2166302.7	62739.1%
497.594	6205.28	-0.0020097	497.594	247800	3.792761	6550029.9	58060629	935564.9%
498.15	6162.43	-0.0020074	498.15	248153	3.789752	7002337.5	61829565	1003231.2%
503.15	6897.49	-0.0019875	503.15	253180	3.838691	12674068	109579918	1588592.7%
503.81	6982	-0.0019849	503.81	253825	3.842734	13718687	118264827	1698906.4%
504.261	6894.76	-0.0019831	504.261	254278	3.838519	14483333	124542773	1807689.9%
505.15	6958.36	-0.0019796	505.15	255177	3.842507	16122203	138233495	1986481.5%

Methanol for Keyes Fit



Methanol Data (Asymptotic)

TRC DATABASES FOR CHEMISTRY AND ENGINEERING TRC SOURCE DATABASE Version 1998-2
 COPYRIGHT (C) 1991-98 TEXAS ENGINEERING EXPERIMENT STATION, TEXAS A&M

Methanol CAS No. Formula
 67-56-1 CH4O MW : 32.04216

$T_c = 512.5$ K $a_0 = 0.99999998$ $a_4 = 5.7431$ $b_0 = -15.08598$
 $P_c = 8060$ kPa $a_1 = 316754.216$ $a_5 = 8.29019366$ $b_1 = 41731.9475$
 $T_1 = 175.59$ K $a_2 = 28.5863597$ $a_6 = -7.1357942$ $\Theta = 0.2$
 $R = 8.314$ $a_3 = 1.91873114$ $a_7 = 2.61395525$ $N = 29.8074732$

Temp (K)	P (kPa)	(T-T ₁)/(T _c -T ₁)	1+(P-P ₁)/(P _c -P ₁)	$\rho_0(t)$	$\rho_{\infty}(t)$	Asymptotic Equation			Error
						dPsat/dT	$\rho(t)^{calc}$	Pcalc	
175.04	0.00016	-0.0016325	1	1	0.02236213	4.1873E-08	1	0.00014625	8.6%
258.54	1.48654	0.24620819	1.000184414	1.00016938	0.44296885	0.00017378	1.00016938	1.36540175	8.1%
285.35	7.2634	0.32578433	1.000901146	1.00098548	0.55866706	0.00082162	1.00098548	7.94313408	9.4%
290.42	11.2471	0.34083286	1.001395402	1.00132313	0.5792983	0.00106292	1.00132313	10.6646254	5.2%
291.15	10.8417	0.34299961	1.001345104	1.00137924	0.5822383	0.00110214	1.00137924	11.1168595	2.5%
292.75	11.3324	0.34774866	1.001405985	1.00150953	0.58865586	0.00119238	1.00150953	12.1669684	7.4%
294.56	14.0335	0.35312101	1.001741109	1.00166972	0.59587284	0.00130187	1.00166973	13.4581757	4.1%
294.95	12.679	0.35427859	1.001573057	1.00170612	0.59742201	0.00132654	1.00170612	13.7515071	8.5%
298.15	17.0226	0.36377668	1.002111965	1.00203173	0.61005619	0.00154412	1.00203174	16.3759967	3.8%
298.2	15.2	0.36392508	1.001885836	1.00203722	0.61025252	0.00154774	1.00203723	16.4202353	8.0%
301.37	20.0522	0.37333412	1.002487846	1.00241257	0.62263508	0.00179242	1.0024126	19.4456767	3.0%
301.65	18.2652	0.37416521	1.002266134	1.00244844	0.62372274	0.0018155	1.00244846	19.7347594	8.0%
325.412	61.2948	0.44489443	1.007604794	1.0077685	0.71303333	0.00490727	1.00776962	62.623298	2.2%
373.1	352.9	0.58623965	1.0437841	1.04933503	0.88809899	0.02355148	1.04957798	369.598641	13.2%
396.483	689.476	0.65564394	1.08554291	1.10273261	0.98438714	0.04345804	1.1039671	837.974996	21.5%
423.15	1392.05	0.73479564	1.172710902	1.21325635	1.11707714	0.07759903	1.21659182	1745.73016	25.4%
453.17	2702.7	0.82389956	1.335322567	1.43433172	1.31604131	0.13378739	1.43790014	3529.47519	30.6%
466.483	3447.38	0.86341456	1.427714629	1.57677081	1.42860261	0.18666769	1.57949437	4670.72489	35.5%
497.594	8205.28	0.95575673	1.769888552	2.04917552	1.77557388	0.26417175	2.05012856	8464.03621	36.4%
498.15	6162.43	0.95740702	1.764569474	2.059664	1.78311456	0.26617182	2.06059783	8548.41691	38.7%
503.15	6897.49	0.97224778	1.855771987	2.15758362	1.85354203	0.28455969	2.15834209	9336.23722	35.4%
503.81	6962	0.97420676	1.863771709	2.17097563	1.88320795	0.28704093	2.17173615	9444.19335	35.7%
504.261	6894.76	0.9755454	1.855429278	2.18020719	1.86986526	0.2887437	2.18095577	9518.5035	38.1%
505.15	6958.36	0.97818408	1.863320097	2.19856358	1.88311476	0.29211744	2.1992894	9666.27255	38.9%

Methanol Data (Asymptotic)

*** C. Triple & Freezing Temp

T_t (K)	Ref.	Key	S
175.22	1929 kel	1	
175.67	1937 stu	0	
175.37	1949 stagup	0	
175.59	1962 car	1	
175.59	1971 carwes	0	
175.61	1985 wilcha	0	

*** A. Critical constants

Property	Value	Units	Reference
P_c	8060	kPa	1988 delpoo 0
P_c	8060	kPa	1990 lydtso 0
T_c	512.5	K	1988 delpoo 0
T_c	512.5	K	1990 lydtso 0

Asymptotic Parm

Small Data Set
with first data point

Gauss	ftc
$b_0 =$	-15.08598
$b_1 =$	-41731.9475
$a_4 =$	5.7431

Marquardt

$b_0 =$ -6407.0141 bad
 $b_1 =$ -89299.592
 $a_4 =$ 3.50301

Newton

$b_0 =$ -479.73755 not horrible
 $b_1 =$ 37924.8477
 $a_4 =$ 4.04111

Gradient

$b_0 =$ -19.99998 not horrible
 $b_1 =$ 20000
 $a_4 =$ 4.04148

DUD ftc

$b_0 =$ -16.8685 not bad
 $b_1 =$ 39120.6223
 $a_4 =$ 4.17904

Small Data Set
without first data point

Gauss
 $b_0 =$ 8020.42101
 $b_1 =$ -68208.523
 $a_4 =$ 4.04099

Marquardt ftc

$b_0 =$
 $b_1 =$
 $a_4 =$

Newton

$b_0 =$ -479.73746
 $b_1 =$ 37924.8436
 $a_4 =$ 4.04111

Gradient

$b_0 =$ -19.99998 not horrible
 $b_1 =$ 20000
 $a_4 =$ 4.04148

DUD ftc

$b_0 =$ -26.97645 pretty good
 $b_1 =$ 41363.3084 over whole
 $a_4 =$ 4.34331 range

Large Data Set
with first data point

Gauss ftc
 $b_0 =$ -91.24942
 $b_1 =$ 47931.2998
 $a_4 =$ 5.79653

Marquardt

$b_0 =$ -6636.1194 bad but gets better with increasing T
 $b_1 =$ -129332.27
 $a_4 =$ 3.5136

Newton

$b_0 =$ -562.01346 not bad great at high T
 $b_1 =$ 51904.2879
 $a_4 =$ 5.36174

Gradient

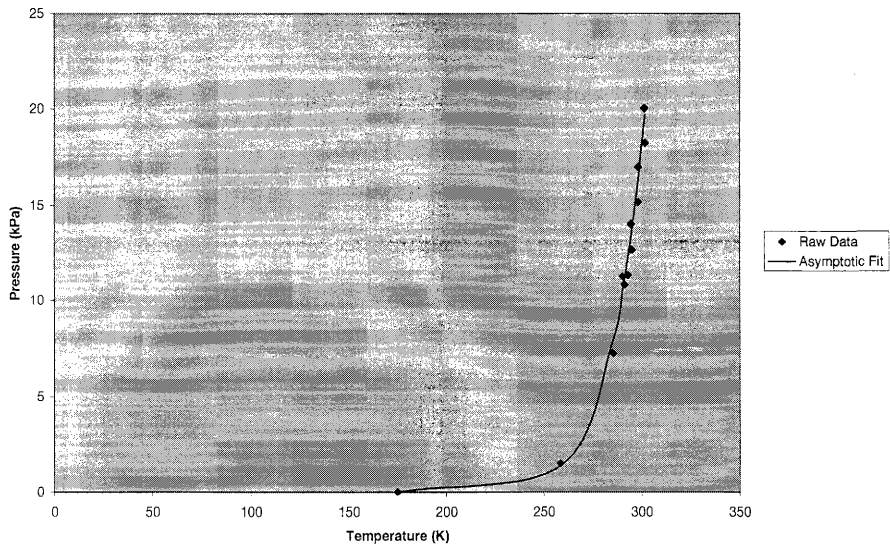
$b_0 =$ -19.99999 great at very low and at
 $b_1 =$ 20000 moderate to high T horrible
 $a_4 =$ 5.3618 in between

DUD

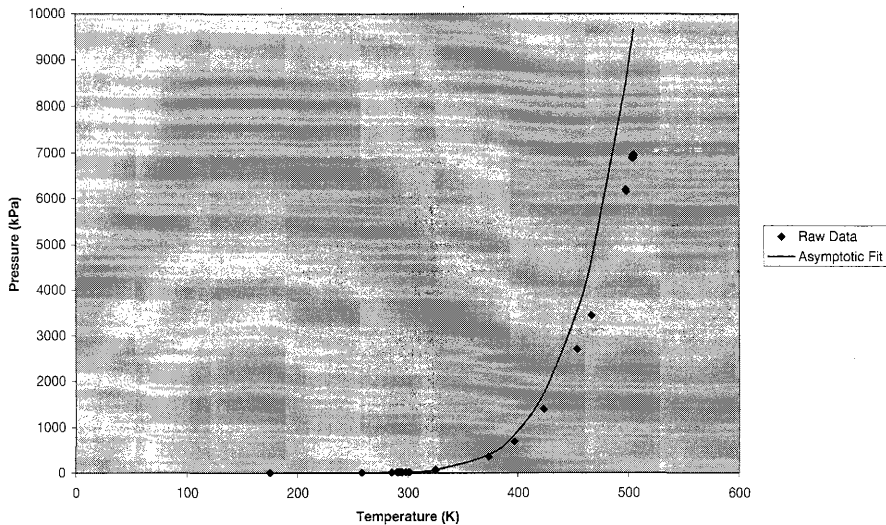
$b_0 =$ 717.37934
 $b_1 =$ -41144.525
 $a_4 =$ 5.36876

*ftc - means failed to converge

Methanol for Asymptotic Fit



Methanol for Asymptotic Fit - Parameters Calculated from low T Extrapolated over Entire Range



Appendix C:
SAS Code and Output

SAS Code

```
Data hall;  
INPUT t 1-12 p 14-28;
```

```
CARDS;
```

```
-0.001632483    1  
0.246208186    1.000184414  
0.325784334    1.000901146  
0.340832863    1.001395402  
0.342999614    1.001345104  
0.347748657    1.001405985  
0.353121012    1.001741109  
0.354278591    1.001573057  
0.363776676    1.002111965  
0.363925084    1.001885836  
0.373334125    1.002487846  
0.374165207    1.002266134
```

```
;
```

```
proc nlin data=hall model=Newton;
```

```
  parms b0=-20. b1=20000. a4=3.5;
```

```
  model p=((2-a4*(1-t)+(-0.11599104+0.29506258*a4**2-0.00021222*a4**5)*(1-  
t)**1.8+(-0.01546028+0.08978160*a4**2-0.05322199*a4**3)*  
(1-t)**3+(0.05725757-0.06817687*a4+0.00047188*a4**5)  
*(1-t)**5)**(87*175.59/512.5)+((1-0.00016/(8060-0.00016))+((0.00016/(8060-  
0.00016))*  
exp((b1/(175.59*8.314)-b0/8.314))*((512.5-175.59)*t/175.59+1)**(b0/8.314)  
*exp((-b1/(8.314*175.59)+b0/8.314)  
/((512.5-175.59)*t/175.59+1)))  
**((87*175.59/512.5)**(512.5/(87*175.59)));
```

```
  output out=tom predicted=pcalc r=diff;
```

```
run;
```

SAS Output

The SAS System 14:54 Sunday, April 18, 1999 1

Non-Linear Least Squares Iterative Phase	Dependent Variable P	Method: Gauss-Newton
Iter	B0 B1 A4	Sum of Squares
0	-20.000000 20000.000000 3.500000	0.000842
1	105.585444 18623.237261 3.500431	0.000841
2	65.332044 24311.159621 3.501417	0.000839
3	-34.121188 33489.909359 3.505063	0.000832
4	-131.190966 42439.242871 3.518709	0.000800
5	-225.738365 51079.712861 3.570522	0.000674
6	-365.154993 63089.469409 3.956458	0.000318
7	-285.225628 56556.932471 4.210997	0.0000252710
8	-178.344902 49389.514191 4.288576	0.0000011221
9	-61.756718 43413.486692 4.380387	0.0000001243
10	-57.266540 43275.155047 4.401894	0.0000001237
11	-52.863559 43137.728807 4.425454	0.0000001233
12	-48.535861 43000.140678 4.451403	0.0000001231
13	-46.408498 42930.882404 4.465761	0.0000001224
14	-44.299587 42861.241223 4.480892	0.0000001218
15	-42.211687 42791.226610 4.496851	0.0000001212
16	-40.148401 42720.893518 4.513693	0.0000001206
17	-38.114349 42650.345922 4.531479	0.0000001201
18	-36.115043 42579.737251 4.550269	0.0000001197
19	-34.156662 42509.266612 4.570136	0.0000001192
20	-32.245725 42439.170224 4.591163	0.0000001188
21	-30.388690 42369.708355 4.613458	0.0000001184
22	-28.591533 42301.149023 4.637166	0.0000001180
23	-26.859361 42233.750633 4.662492	0.0000001176
24	-25.186128 42167.745996 4.689735	0.0000001173
25	-23.604480 42103.329889 4.719337	0.0000001169
26	-22.085750 42040.651416 4.751978	0.0000001166
27	-20.640086 41979.811426 4.788742	0.0000001163
28	-19.266699 41920.864471 4.831468	0.0000001161
29	-17.964221 41863.824831 4.883591	0.0000001159
30	-16.731274 41808.678258 4.952543	0.0000001159
31	-16.149487 41782.045465 5.005807	0.0000001157
32	-15.587048 41755.911717 5.084187	0.0000001156
33	-15.317114 41743.136635 5.159228	0.0000001156
34	-15.186550 41736.866867 5.235831	0.0000001155
35	-15.123392 41733.795394 5.323328	0.0000001155
36	-15.093083 41732.303018 5.451474	0.0000001155
37	-15.086025 41731.949880 5.658275	0.0000001155
38	-15.085977 41731.947521 5.743104	0.0000001155

WARNING: Step size shows no improvement.
 WARNING: PROC NLIN failed to converge.

Non-Linear Least Squares Summary Statistics		Dependent Variable P
Source	DF Sum of Squares	Mean Square
Regression	3 12.034627307	4.011542436
Residual	9 0.000000116	0.000000013
Uncorrected Total	12 12.034627423	
(Corrected Total)	11 0.000006492	

WARNING: PROC NLIN failed to converge.

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval	
			Lower	Upper
B0	-15.08598	0	-15.085977	-15.085977
B1	41731.94752	0	41731.947521	41731.947521
A4	5.74310	0	5.743104	5.743104

Asymptotic Correlation Matrix

Corr	B0	B1	A4
B0	1	-0.999742169	0.8920138098
B1	-0.999742169	1	-0.883669362
A4	0.8920138098	-0.883669362	1

Appendix D:
Maple Worksheets

1

```
> restart:with(linalg):
Warning, new definition for norm
Warning, new definition for trace
Antione's E.O.S.
```

```
> Antione:=exp(A-B/(T+C));
```

$$\text{Antione} := e^{\left(A - \frac{B}{T+C}\right)}$$

```
> Dantione:=diff(Antione,T);
```

$$\text{Dantione} := \frac{B e^{\left(A - \frac{B}{T+C}\right)}}{(T+C)^2}$$

```
> d2antione:=diff(Dantione,T);
```

$$\text{d2antione} := -2 \frac{B e^{\left(A - \frac{B}{T+C}\right)}}{(T+C)^3} + \frac{B^2 e^{\left(A - \frac{B}{T+C}\right)}}{(T+C)^4}$$

For slope of the Antione E.O.S. to change signs, it must first go through zero.

Because exp(#) will never be equal to zero just very close, we will focus on the B/(T+C)^2 term

```
> eq1:=0=B/(T+C)^2;Adsoln:=B=0;
```

$$\text{eq1} := 0 = \frac{B}{(T+C)^2}$$

$$\text{Adsoln} := B = 0$$

The second derivative must go through zero if the concavity is going to change.

```
> eq2:=0=-2*B/(T+C)^3+(B/(T+C))^2;Ad2soln:=solve(eq2,T);
```

$$\text{eq2} := 0 = -2 \frac{B}{(T+C)^3} + \frac{B^2}{(T+C)^2}$$

$$\text{Ad2soln} := -\frac{-2+BC}{B}$$

Keyes E.O.S.

```
> Keyes:=10^(-A/T+C*T+D*T^2+E);
```

$$\text{Keyes} := 10^{\left(-\frac{A}{T} + CT + DT^2 + E\right)}$$

```
> Dkeyes:=diff(Keyes,T);
```

$$\text{Dkeyes} := 10^{\left(-\frac{A}{T} + CT + DT^2 + E\right)} \left(\frac{A}{T^2} + C + 2DT \right) \ln(10)$$

```
> d2keyes:=diff(Dkeyes,T);
```

d2keyes :=

$$10^{\left(-\frac{A}{T} + CT + DT^2 + E\right)} \left(\frac{A}{T^2} + C + 2DT \right)^2 \ln(10)^2 + 10^{\left(-\frac{A}{T} + CT + DT^2 + E\right)} \left(-2 \frac{A}{T^3} + 2D \right) \ln(10)$$

Using the same arguments above

> eq3:=0=A/T^2+C+2*D*T;Kdsoln:=solve(eq3,T);

$$eq3 := 0 = \frac{A}{T^2} + C + 2DT$$

$$Kdsoln := \frac{1 \%1^{1/3}}{6 D} + \frac{1}{6 D} \frac{C^2}{\%1^{1/3}} - \frac{1}{6 D} C - \frac{1}{12} \frac{\%1^{1/3}}{D} - \frac{1}{12} \frac{C^2}{D \%1^{1/3}} - \frac{1}{6} \frac{C}{D} + \frac{1}{2} I \sqrt{3} \left(\frac{1}{6} \frac{\%1^{1/3}}{D} - \frac{1}{6} \frac{C^2}{D \%1^{1/3}} \right) - \frac{1}{12} \frac{\%1^{1/3}}{D} - \frac{1}{12} \frac{C^2}{D \%1^{1/3}} - \frac{1}{6} \frac{C}{D} - \frac{1}{2} I \sqrt{3} \left(\frac{1}{6} \frac{\%1^{1/3}}{D} - \frac{1}{6} \frac{C^2}{D \%1^{1/3}} \right)$$

$$\%1 := -54 A D^2 - C^3 + 6 \sqrt{3} \sqrt{A (27 A D^2 + C^3)} D$$

We will only consider the real root, the first one given

The same will be computed for the second derivative

> eq4:=0=(A/T^2+C+2*D*T)^2*ln(10)+(-2*A/T^3+2*D);Kd2soln:=solve(eq4,T);

$$eq4 := 0 = \left(\frac{A}{T^2} + C + 2DT \right)^2 \ln(10) - 2 \frac{A}{T^3} + 2D$$

$$Kd2soln := \text{RootOf}(4 \ln(10) D^2 _Z^6 + 4 \ln(10) C _Z^5 D + (\ln(10) C^2 + 2D) _Z^4 + 4 \ln(10) A D _Z^3 + 2 \ln(10) A C _Z^2 - 2 _Z A + \ln(10) A^2)$$

Wagner E.O.S.

> Wagner:=exp((A*tau+B*tau^1.5+C*tau^3+D*tau^6)/(1-tau));

$$Wagner := e^{\left(\frac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{1-\tau} \right)}$$

> Dwagner:=diff(Wagner,tau);

$$Dwagner := \left(\frac{A + 1.5 B \tau^{0.5} + 3 C \tau^2 + 6 D \tau^5}{1-\tau} + \frac{A \tau + B \tau^{1.5} + C \tau^3 + D \tau^6}{(1-\tau)^2} \right) e^{\left(\frac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{1-\tau} \right)}$$

> d2wagner:=diff(Dwagner,tau);

$$d2wagner := \left(\frac{.75 \frac{B}{\tau^5} + 6 C \tau + 30 D \tau^4}{1-\tau} + 2 \frac{A + 1.5 B \tau^{0.5} + 3 C \tau^2 + 6 D \tau^5}{(1-\tau)^2} + 2 \frac{\%1}{(1-\tau)^3} \right) e^{\left(\frac{\%1}{1-\tau} \right)} + \left(\frac{A + 1.5 B \tau^{0.5} + 3 C \tau^2 + 6 D \tau^5}{1-\tau} + \frac{\%1}{(1-\tau)^2} \right)^2 e^{\left(\frac{\%1}{1-\tau} \right)}$$

$$\%1 := A \tau + B \tau^{1.5} + C \tau^3 + D \tau^6$$

Use same argument as above to simplify

> eq5:=0=Dwagner/Wagner;simplify(eq5);Wdsoln:=solve(eq5,tau);

$$eq5 := 0 = \frac{A + 1.5 B \tau^5 + 3 C \tau^2 + 6 D \tau^5}{1 - \tau} + \frac{A \tau + B \tau^{1.5} + C \tau^3 + D \tau^6}{(1 - \tau)^2}$$

$$0 = -5000000000 \frac{-2. A - 3. B \sqrt{\tau} + B \tau^{3/2} - 6. C \tau^2 + 4. C \tau^3 - 12. D \tau^5 + 10. D \tau^6}{(-1. - \tau)^2}$$

$$Wdsoln := \text{RootOf}(-2 A - 3 B _Z + B _Z^3 - 6 C _Z^4 + 4 C _Z^6 - 12 D _Z^{10} + 10 D _Z^{12})^2$$

Same for second deriv to check concavity

> eq6:=0=(.75*B/tau^.5+6*C*tau+30*D*tau^4)/(1-tau)+2*(A+1.5*B*tau^.5+3*C*tau^2+6*D*tau^5)/(1-tau)^2+2*(A*tau+B*tau^1.5+C*tau^3+D*tau^6)/(1-tau)^3+(A+1.5*B*tau^.5+3*C*tau^2+6*D*tau^5)/(1-tau)+(A*tau+B*tau^1.5+C*tau^3+D*tau^6)/(1-tau)^2;Wd2soln:=solve(eq6,tau);

$$eq6 = 0 = \frac{.75 \frac{B}{\tau^5} + 6 C \tau + 30 D \tau^4}{1 - \tau} + 2 \frac{A + 1.5 B \tau^5 + 3 C \tau^2 + 6 D \tau^5}{(1 - \tau)^2}$$

$$+ 2 \frac{A \tau + B \tau^{1.5} + C \tau^3 + D \tau^6}{(1 - \tau)^3} + \left(\frac{A + 1.5 B \tau^5 + 3 C \tau^2 + 6 D \tau^5}{1 - \tau} + \frac{A \tau + B \tau^{1.5} + C \tau^3 + D \tau^6}{(1 - \tau)^2} \right)^2$$

$$Wd2soln := \text{RootOf}(100 _Z^{25} D^2 - 240 _Z^{23} D^2 + 144 _Z^{21} D^2 + 80 _Z^{19} C D - 216 _Z^{17} C D + 20 D _Z^{16} B + (144 C D - 80 D) _Z^{15} - 84 B _Z^{14} D + (272 D - 40 A D + 16 C^2) _Z^{13} + 72 B _Z^{12} D + (-312 D + 48 A D - 48 C^2) _Z^{11} + 8 C _Z^{10} B + (36 C^2 - 8 C + 120 D) _Z^9 - 36 C _Z^8 B + (32 C - 16 A C + B^2) _Z^7 + (36 B C + B) _Z^6 + (-48 C + 24 A C - 6 B^2) _Z^5 + (-7 B - 4 A B) _Z^4 + (-8 A + 24 C + 9 B^2) _Z^3 + (12 A B + 3 B) _Z^2 + (4 A^2 + 8 A) _Z + 3 B)^2$$

Asymptotic E.O.S.

> p_triple:=a[0]+a[1]*(a[3]*t+1)^(b[0]/R)*exp((-a[2]+b[0]/R)/(a[3]*t+1));

$$p_triple := a_0 + a_1 (a_3 t + 1) e^{\left(\frac{b_0}{R} \right) \left(\frac{-a_2 + \frac{b_0}{R}}{a_3 t + 1} \right)}$$

> p_infinity:=2-a[4]*(1-t)+a[5]*(1-t)^(2-Theta)+a[6]*(1-t)^3+a[7]*(1-t)^4;

$$p_infinity := 2 - a_4 (1 - t) + a_5 (1 - t)^{(2 - \Theta)} + a_6 (1 - t)^3 + a_7 (1 - t)^4$$

> Hall:=(p_triple^N+p_infinity^N)^(1/N);

$$\text{Hall} := \left(\left(a_0 + a_1 (a_3 t + 1) \left(\frac{b_0}{R} \right) e^{\left(\frac{-a_2 + \frac{b_0}{R}}{a_3 t + 1} \right)^N} \right) + (2 - a_4 (1 - t) + a_5 (1 - t)^{(2 - \Theta)} + a_6 (1 - t)^3 + a_7 (1 - t)^4)^N \right)^{\left(\frac{1}{N} \right)}$$

> Dhall := diff(Hall, t);

$$\text{Dhall} := (\%4^N + \%1^N)^{\left(\frac{1}{N} \right)} \left(\frac{\%4^N N \left(\frac{a_1 \%3 b_0 a_3 \%2}{R (a_3 t + 1)} - \frac{a_1 \%3 \left(-a_2 + \frac{b_0}{R} \right) a_3 \%2}{(a_3 t + 1)^2} \right)}{\%4} + \frac{\%1^N N \left(a_4 - \frac{a_5 (1 - t)^{(2 - \Theta)} (2 - \Theta)}{1 - t} - 3 a_6 (1 - t)^2 - 4 a_7 (1 - t)^3 \right)}{\%1} \right) / (N (\%4^N + \%1^N))$$

$$\%1 := 2 - a_4 (1 - t) + a_5 (1 - t)^{(2 - \Theta)} + a_6 (1 - t)^3 + a_7 (1 - t)^4$$

$$\%2 := e^{\left(\frac{-a_2 + \frac{b_0}{R}}{a_3 t + 1} \right)}$$

$$\%3 := (a_3 t + 1)^{\left(\frac{b_0}{R} \right)}$$

$$\%4 := a_0 + a_1 \%3 \%2$$

> d2hall := diff(Dhall, t);

$$\text{d2hall} := \frac{(\%4^N + \%1^N)^{\left(\frac{1}{N} \right)} \left(\frac{\%4^N N \%6}{\%4} + \frac{\%1^N N \%5}{\%1} \right)^2}{N^2 (\%4^N + \%1^N)^2} + (\%4^N + \%1^N)^{\left(\frac{1}{N} \right)} \left(\frac{\%4^N N^2 \%6^2}{\%4^2} + \%4^N N \left(\frac{a_1 \%3 b_0^2 a_3^2 \%2}{R^2 (a_3 t + 1)^2} - \frac{a_1 \%3 b_0 a_3^2 \%2}{R (a_3 t + 1)^2} - 2 \frac{a_1 \%3 b_0 a_3^2 \left(-a_2 + \frac{b_0}{R} \right) \%2}{R (a_3 t + 1)^3} \right) \right)$$

$$\begin{aligned}
& + 2 \left(\frac{a_1 \%3 \left(-a_2 + \frac{b_0}{R} \right) a_3^2 \%2}{(a_3 t + 1)^3} + \frac{a_1 \%3 \left(-a_2 + \frac{b_0}{R} \right)^2 a_3^2 \%2}{(a_3 t + 1)^4} \right) / (\%4) - \frac{\%4^N N \%6^2}{\%4^2} \\
& + \frac{\%1^N N^2 \%5^2}{\%1^2} \\
& + \frac{\%1^N N \left(\frac{a_5 (1-t)^{(2-\Theta)} (2-\Theta)^2}{(1-t)^2} - \frac{a_5 (1-t)^{(2-\Theta)} (2-\Theta)}{(1-t)^2} + 6 a_6 (1-t) + 12 a_7 (1-t)^2 \right)}{\%1} \\
& - \frac{\%1^N N \%5^2}{\%1^2} \left/ \left(N (\%4^N + \%1^N) - \frac{(\%4^N + \%1^N) \left(\frac{1}{N} \right) \left(\frac{\%4^N N \%6}{\%4} + \frac{\%1^N N \%5}{\%1} \right)^2}{N (\%4^N + \%1^N)^2} \right) \right. \\
\%1 & := 2 - a_4 (1-t) + a_5 (1-t)^{(2-\Theta)} + a_6 (1-t)^3 + a_7 (1-t)^4 \\
\%2 & := e \begin{pmatrix} \frac{b_0}{R} \\ -a_2 + \frac{b_0}{R} \\ a_3 t + 1 \end{pmatrix} \\
\%3 & := (a_3 t + 1) \begin{pmatrix} \frac{b_0}{R} \end{pmatrix} \\
\%4 & := a_0 + a_1 \%3 \%2 \\
\%5 & := a_4 - \frac{a_5 (1-t)^{(2-\Theta)} (2-\Theta)}{1-t} - 3 a_6 (1-t)^2 - 4 a_7 (1-t)^3 \\
\%6 & := \frac{a_1 \%3 b_0 a_3 \%2}{R (a_3 t + 1)} - \frac{a_1 \%3 \left(-a_2 + \frac{b_0}{R} \right) a_3 \%2}{(a_3 t + 1)^2}
\end{aligned}$$