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# On the linearization of Antoine's law

## Short Note

### Pascal Floquet

#### Abstract

A multivariate linearized Antoine's equation (*MLAE*) is presented in this short note. To our knowledge, it is the first time this multi-linear equation is proposed in the literature. Compared with initial null parameters or « Clapeyron » type initial parameters, that do not take into account the highly non-linear correlation between the parameters  $B$  and  $C$ , our procedure gives a very good initial guess for the non-linear regression of vapor pressure *versus* temperature. Fortunately, the multi-linear expression of linearized Antoine's law is obtained in a simple, non iterative manner. Examples relevant from thermodynamical literature are used to show the quality of our *MLAE* parameters in order to converge to non-linear regression solution of Antoine's model and to compare our approach with the classical ones.

#### Introduction

Historically, many different formulas and graphical representations have been suggested for the vapor pressure-temperature relationship for a pure component [Wisniak, 2001]. Clapeyron's formula proposed in 1834 and thermodynamically stated by Clausius in 1864 gave birth to the well-known Clausius-Clapeyron differential relationship

$$\frac{d \ln P^\circ}{d\left(\frac{1}{T}\right)} = \frac{-\Delta H^v}{R\Delta z} \quad (1)$$

Where  $\Delta H^v$  is the latent heat of vaporization,  $z = \frac{P^\circ v}{RT}$  the compressibility factor,  $P^\circ$ ,  $v$  and  $T$  respectively the vapor pressure, the corresponding volume and the temperature. When  $\frac{\Delta H^v}{\Delta z}$  is assumed to be constant, it leads to

$$\log P^\circ = A - \frac{B}{T} \quad (2)$$

This assumption, or a stronger one of constant heat of vaporization, was soon found to be one of the main reasons why the Clausius-Clapeyron equation would only fit the experimental data in a limited temperature range. A common way to improve the fitting ability is to use the Antoine's equation for the vapor pressure of a saturated liquid which introduces a third parameter  $C$  in the approximated Clausius-Clapeyron equation

$$\log P^\circ = A - \frac{B}{T + C} \quad (3)$$

Classically, the three coefficients  $A$ ,  $B$  and  $C$  have to be determined thanks to experimental data. From a numerical point of view, the equation (2) is clearly linear with the coefficients  $A$  and  $B$ , in terms of  $\log P^\circ$  and  $1/T$  variables; thus, if a substance behaves according to the Clausius-Clapeyron model, a plot of  $\log P^\circ$  against  $1/T$  should yield a straight line with slope  $-B$ . On the contrary, Antoine's equation (3) is a non-linear equation with respect to parameters  $A$ ,  $B$  and  $C$  and for the same variables  $\log P^\circ$  and  $1/T$ . This equation is a well-known non-linear model in the field of Chemical Engineering education and often used as an example for identification purpose of non-linear model [Corriou, 2004].

We propose, in this work, to promote a change of variables leading to a linearized Antoine's equation. It is easy, with this model, to compute the above coefficients  $A$ ,  $B$  and  $C$  *via* a classical linear regression method. Thus, these values of coefficients are good candidates for initial points of a non-linear regression of complete non-linear Antoine's law. To prove the adequacy of a such initial guess, three examples have

been chosen with experimental value ( $T_{exp}$ ,  $P_{exp}$ ) of temperature and vapor pressure: carbon tetrachloride  $CCl_4$  [Hildebrand and Mc Donald *in* Boublik *et al.*, 1973], di-isobutyl hexahydrophthalate (DIBE) [Liu *et al.*, 2005] and 2,6,10,14-tetramethylpentadecane (Pristane) [Bourasseau *et al.*, 2004].

### Several Non-linear Regressions on Antoine's Law

The non-linear Antoine's model (3) can be fitted with experimental data *via* a lot of distinct criteria to be minimized. Classical ones are the following:

$$\text{Logarithmic Absolute criterion (LAC)} \sum_{i=1}^{n_{exp}} (\log P_{exp}^{\circ} - \log P_{calc}^{\circ})^2 = \sum_{i=1}^{n_{exp}} \left( \log P_{exp}^{\circ} - \left( A - \frac{B}{T_{exp} + C} \right) \right)^2$$

$$\text{Logarithmic Relative criterion (LRC)} \sum_{i=1}^{n_{exp}} \left( \frac{\log P_{exp}^{\circ} - \log P_{calc}^{\circ}}{\log P_{exp}^{\circ}} \right)^2 = \sum_{i=1}^{n_{exp}} \left( \frac{\log P_{exp}^{\circ} - \left( A - \frac{B}{T_{exp} + C} \right)}{\log P_{exp}^{\circ}} \right)^2$$

$$\text{Absolute criterion (AC)} \sum_{i=1}^{n_{exp}} (P_{exp}^{\circ} - P_{calc}^{\circ})^2 = \sum_{i=1}^{n_{exp}} \left( P_{exp}^{\circ} - e^{A - \frac{B}{T_{exp} + C}} \right)^2$$

$$\text{Relative criterion (RC)} \sum_{i=1}^{n_{exp}} \left( \frac{P_{exp}^{\circ} - P_{calc}^{\circ}}{P_{exp}^{\circ}} \right)^2 = \sum_{i=1}^{n_{exp}} \left( \frac{P_{exp}^{\circ} - e^{A - \frac{B}{T_{exp} + C}}}{P_{exp}^{\circ}} \right)^2$$

$$\text{Boublik } et al. \text{ criterion (BC)} \sum_{i=1}^{n_{exp}} ((\log P_{exp}^{\circ} - A)(T_{exp} + C) + B)^2$$

All these criteria deal with least-square minimization problems that are not exactly equivalent in terms of parameter solutions or final criterion value. In this work, all the least-square fitting are performed with lsqnonlin program proceeding from Matlab<sup>®</sup> Optimization Toolbox, based on the Levenberg-Marquardt method with line search for medium-scale problem [Levenberg, 1944; Marquardt, 1963]. For comparison purpose, the tolerances associated with these problems (termination tolerance on the function value  $\varepsilon_F$  and on variable change  $\varepsilon_X^1$ ) are set to  $10^{-7}$ .

### Interaction between C and D coefficients

The difficulties of non-linear regression procedures (LAC, LRC, AC, RC, BC or other criteria) arise from the correlation between  $B$  and  $C$  coefficients and from the number of local minima of the optimization problem. As an example, it can be seen, for the carbon tetrachloride  $CCl_4$  [Boublik *et al.*, 1973] example and for a fixed value of coefficient  $A$  ( $A = 15$ ), the response surface (criterion AC) *versus*  $B$  and  $C$  values. It can be observed that the "minimum valley" is quite narrow and may explain the numerical difficulties encountered.

<sup>1</sup> Three termination criteria have been applied: non evolution on variables (evolution less than  $\varepsilon_X$ ), non evolution of least-square function (evolution less than  $\varepsilon_F$ ) and first-order optimality conditions less than  $\varepsilon_F$ .

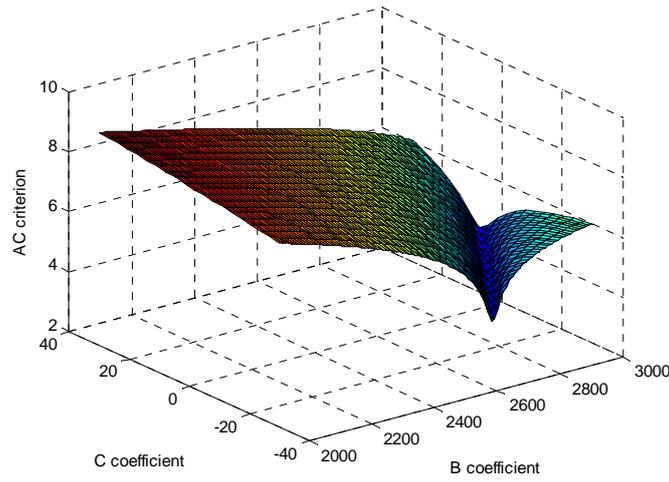


Figure 1: Values of AC criterion *versus* coefficients  $B$  and  $C$  ( $A = 15$ ) for the  $\text{CCl}_4$  example  
 A good initial point of the regression procedure provides us a less difficult path tracing to the solution and a clear advantage in terms of global minimum localization.

### Several Initial Points for the Non-linear Regression

All the non-linear regressions are performed with the following initial points:

- “Null” initial point: all the initial coefficient values  $A$ ,  $B$  and  $C$  are set to zero;
- “Clapeyron” initial point: initial coefficient values  $A$  and  $B$  are set to the solution of the linear Clausius-Clapeyron equation (2); the initial value of  $C$  is equal to zero;
- “Linearized Antoine” initial point: all the initial coefficient values  $A$ ,  $B$  and  $C$  are set to the solution of the linearized Antoine equation below.

This new linear initial point we proposed is obtained by the following transformation of Antoine equation (3):

$$\log P^\circ = \frac{AT + AC - B}{T + C} \Rightarrow C \log P^\circ = AT - T \log P^\circ + (AC - B)$$

$$\Downarrow$$

$$\log P^\circ = \left(A - \frac{B}{C}\right) + \frac{A}{C}T - \frac{T \log P^\circ}{C} \quad (4)$$

This equation (4) is linear with the coefficients  $A/C$ ,  $-1/C$  and  $(A - B/C)$ , in terms of transformed variables  $\log P^\circ$ ,  $T$  and  $T \log P^\circ$ . It is then possible to linearly identify these coefficients and, thus, the original ones  $A$ ,  $B$  and  $C$ , by fitting  $\log P^\circ_{exp}$  with  $T_{exp}$  and  $T_{exp} \log P^\circ_{exp}$ .

If we note  $X$  the following ( $n_{exp} \times 3$ ) matrix  $X = \begin{pmatrix} 1 & T_{exp}^1 & T_{exp}^1 \log P_{exp}^{o1} \\ 1 & T_{exp}^2 & T_{exp}^2 \log P_{exp}^{o2} \\ \dots & \dots & \dots \\ 1 & T_{exp}^{n_{exp}} & T_{exp}^{n_{exp}} \log P_{exp}^{on_{exp}} \end{pmatrix}$  and  $Y$  the following array

$$Y = \begin{pmatrix} \log P_{exp}^{o1} \\ \log P_{exp}^{o2} \\ \dots \\ \log P_{exp}^{on_{exp}} \end{pmatrix}, \text{ then the multi-linear least-square regression gives the coefficient array } \beta = \begin{pmatrix} A - \frac{B}{C} \\ \frac{A}{C} \\ \frac{-1}{C} \end{pmatrix}$$

by

$$\beta = (X^T X)^{-1} X^T Y$$

Then

$$\begin{cases} A = -\frac{\beta_2}{\beta_3} \\ B = \frac{\beta_2}{\beta_3^2} + \frac{\beta_1}{\beta_3} \\ C = -\frac{1}{\beta_3} \end{cases}$$

The adequation of the linearized model can be seen in the following figure that gives the response  $\log P^\circ$  with  $T$  and  $T \log P^\circ$  for the Pristane example. Scatter points are experimental points and surface corresponds to the multi-linear model.

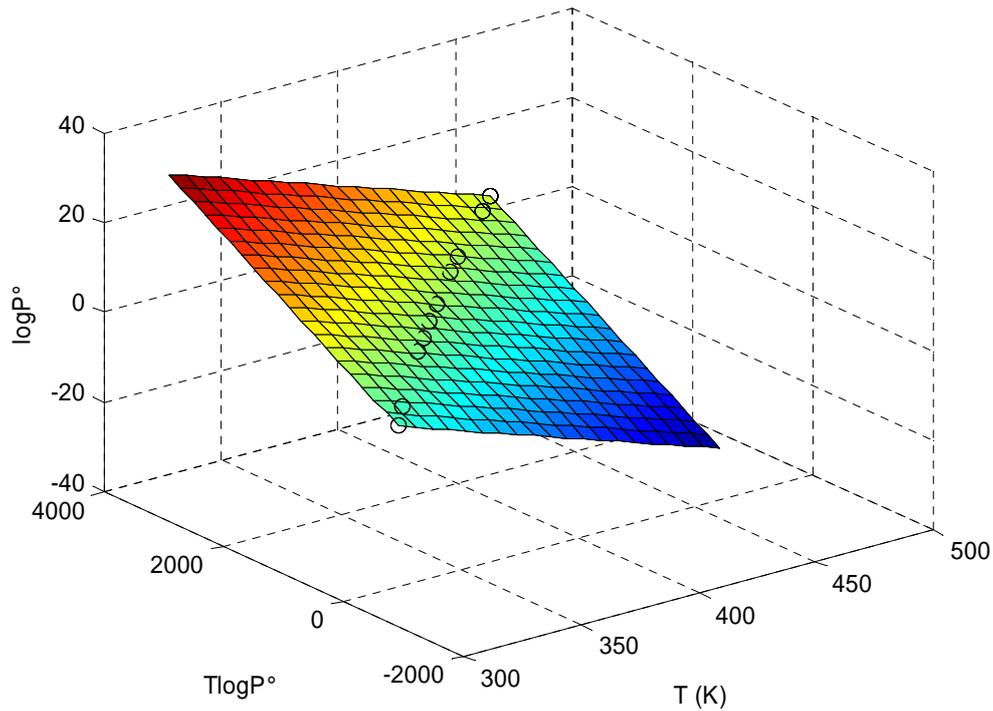


Figure 2: Values of response  $\log P^\circ$  with  $T$  and  $T \log P^\circ$  for the Pristane example

The table 1 shows the complete non-linear regression results for all the criteria and examples, in terms of coefficient initialization.

It is easy to see that our *MLAE* initialization procedure gives in all cases better results compared with other initialization methods. The convergence of the non-linear regression to optimal solution with the different initializations is shown, for the DIBE example and the LAC criterion, in the following figure.

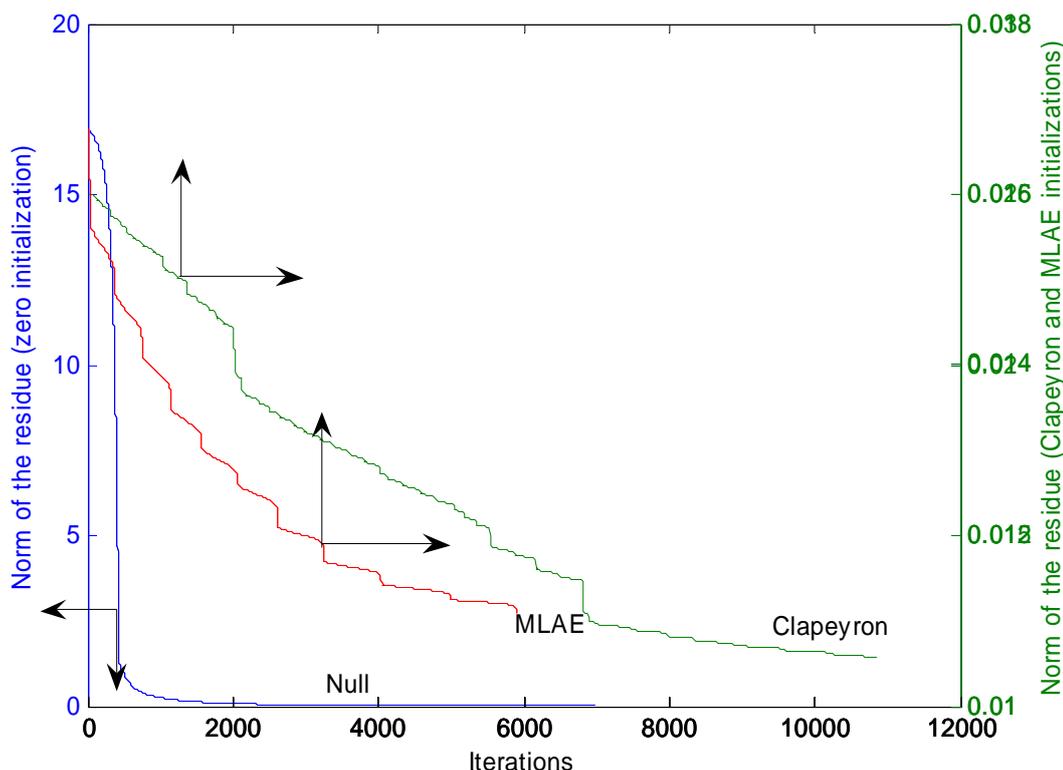


Figure 3: Convergence *versus* Initialization for the DIBE example and the RC criterion (Null Initialization: left Y axis, Clapeyron and *MLAE* Initializations: right Y axis)

As foreseen, the proposed *MLAE* procedure is quite good for quickly converge to optimal solution. The table 2 shows the literature results and the criterion chosen. In all the case, the initialization proposed and the non-linear regression end to the same or better solution.

## Conclusion and Significance

A new linearized Antoine equation is proposed to initialize the well-known Antoine's regression problem. This equation is easy to compute and allows to obtain quickly good results to the non-linear regression of vapor pressure *versus* temperature of pure component.

## Notations

$P^{\circ}$	Vapor pressure
$A$	First Antoine's coefficient
$B$	Second Antoine's coefficient
$C$	Third Antoine's coefficient
$T$	Temperature (K)
$X$	Experiment matrix ( $n_{exp} \times 3$ )
$Y$	Response array ( $n_{exp} \times 1$ )
<u>Acronym</u>	
AC	Absolute Criterion
BC	Boublik's Criterion
<i>MLAE</i>	Multivariate Linearized Antoine's Equation
DIBE	Di-IsoButyl hExahydroptalate
LAC	Logarithmic Absolute Criterion
LRC	Logarithmic Relative Criterion
RC	Relative Criterion
<u>Greek Letters</u>	
$\beta$	Parameter array ( $3 \times 1$ )
$\Delta V$	Volume change

$\Delta H$	Heat of vaporization
$\varepsilon_X$	termination tolerance on the variable change (least-square procedure)
$\varepsilon_F$	termination tolerance on the function value (least-square procedure)
<u>Subscript</u>	
exp	experimental
calc	calculated

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Criterion	Initialization	CCI4					DIBE					Pristane				
		A	B	C	Norm	Iterations (Function evaluations)	A	B	C	Norm	Iterations (Function evaluations)	A	B	C	Norm	Iterations (Function evaluations)
<i>MLAE</i>		<b>15.8502</b>	<b>2794.9</b>	<b>-46.64</b>			<b>11.4945</b>	<b>2658.0</b>	<b>-209.45</b>			<b>20.4388</b>	<b>4274.8</b>	<b>-116.09</b>		
<b>LAC</b>	Zero	15.872	2807.1	-46.041	$6.06 \cdot 10^{-6}$	39 (298)	13.394	3817.6	-154.95	$1.09 \cdot 10^{-2}$	88 (684)	20.479	4296.8	-115.42	$1.12 \cdot 10^{-3}$	57 (440)
	Clapeyron	17.567	3824.4	-0.026	$2.50 \cdot 10^{-4}$	2 (12)	13.394	3817.6	-154.95	$1.09 \cdot 10^{-2}$	122 (943)	20.479	4296.8	-115.42	$1.12 \cdot 10^{-3}$	58 (445)
	Antoine Linear	15.850	2794.9	-46.638	$6.12 \cdot 10^{-6}$	2 (12)	13.394	3817.6	-154.95	$1.09 \cdot 10^{-2}$	49 (377)	20.438	4274.8	-116.07	$1.14 \cdot 10^{-3}$	3 (19)
<b>LRC</b>	Zero	13.393	1606.8	-112.460	$4.14 \cdot 10^{-5}$	85 (664)	9.606	1768.1	-256.00	$1.32 \cdot 10^{-2}$	88 (671)	20.360	4242.1	-116.79	$1.80 \cdot 10^{-4}$	578 (4304)
	Clapeyron	17.346	3678.2	-6.436	$6.94 \cdot 10^{-6}$	9 (65)	9.606	1768.1	-256.00	$1.32 \cdot 10^{-2}$	176 (1348)	20.360	4242.1	-116.79	$1.80 \cdot 10^{-4}$	418 (3147)
	Antoine Linear	15.850	2794.9	-46.638	$1.83 \cdot 10^{-7}$	2 (12)	9.606	1768.1	-256.00	$1.32 \cdot 10^{-2}$	49 (371)	20.360	4242.1	-116.79	$1.80 \cdot 10^{-4}$	21 (154)
<b>AC</b>	Zero	16.020	2890.5	-41.925	0.939	234 (1770)	13.254	3681.1	-163.13	0.236	188 (1433)	NON CONVERGENCE				
	Clapeyron	16.020	2890.5	-41.925	0.939	108 (816)	13.254	3681.1	-163.13	0.236	248 (1897)	26.276	8647.3	13.91	28.424	1524 (6100)
	Antoine Linear	16.020	2890.5	-41.925	0.939	24 (197)	13.254	3681.1	-163.13	0.236	70 (522)	23.998	6726.6	-38.82	28.820	2466 (9868)
<b>RC</b>	Zero	16.000	2879.2	-42.488	0.024	220 (1681)	14.024	4251.5	-136.51	0.109	134 (1038)	NON CONVERGENCE				
	Clapeyron	16.000	2879.2	-42.488	0.024	95 (730)	14.024	4251.5	-136.51	0.109	131 (1004)	21.603	4938.5	-96.33	5.198	25000 (100004)*
	Antoine Linear	16.000	2879.2	-42.488	0.024	25 (202)	14.024	4251.5	-136.51	0.109	59 (446)	21.123	4657.6	-104.59	4.912	16534 (66140)
<b>BC</b>	Zero	15.883	2813.3	-45.739	0.472	224 (1699)	12.869	3475.2	-170.10	31.550	7949 (31800)	20.459	4285.5	-115.76	9.807	7295 (29184)
	Clapeyron	15.883	2813.3	-45.739	0.472	57 (441)	12.901	3495.4	-169.19	31.551	20878 (83512)	20.460	4286.3	-115.74	9.807	17647 (70592)
	Antoine Linear	15.883	2813.3	-45.739	0.472	11 (80)	12.878	3481.4	-169.82	31.550	16641 (66568)	20.458	4285.5	-115.76	9.807	393 (1576)

Table 1: Comparison of initialization techniques on Antoine regression problem with several criteria (\* maximal number of function calls)

Criterion	CCI4			DIBE			Pristane		
	A	B	C	A	B	C	A	B	C
	15.938	2844.1	-44.213	12,866	3471,6	-170,35	20,489	4301,7	-115,26
<b>LAC</b>	$2.58 \cdot 10^{-3}$			$1.06 \cdot 10^{-1}$			$3.37 \cdot 10^{-2}$		
<b>LRC</b>	$4.79 \cdot 10^{-4}$			$1.80 \cdot 10^{-1}$			$2.97 \cdot 10^{-1}$		
<b>AC</b>	0.9974			0.69629			41.129		
<b>RC</b>	0.1596			0.37515			5.5148		
<b>BC</b>	0.7093			31.56			9.8759		

Table2: Literature results (norm of the criterion) on Antoine regression problem with several criteria (in grey, the criterion chosen by the authors, if known)