Evaluation and prediction of latent heat of vaporization at various temperatures for pure component

Engi.Mohammed jabbar ajrash , Prof. Dr.mahmod omer abdallah,
Ministry of Oil, Midland Refinery Co.   Nahrain University
Iraq –Baghdad   Iraq-Baghdad
Mohammedkony@yahoo.com

Abstract

The prediction of latent heat of vaporization of pure compounds has at least sixteen methods. All these methods has been evaluated in this work, There are at least nine methods available in literature for prediction of latent heat of vaporization at any temperature using either vapor pressure data or the law of corresponding states .These methods predict the latent heat of vaporization at various temperatures directly. Halim and stiel is the best method among these nine methods which is directly deal with polarity of compounds by introducing what is known polarity factor of polar compounds and it gives 1.**552** absolute average deviation percent compared with experimental data for 18 pure non polar compounds and 446 data points .On the other hand it gives **2.8476** AAD% compared with experimental data for 6 polar compounds and 180 data points .

The prediction of the latent heat of vaporization from normal boiling point have at least seven methods. Riedel at normal boiling method have the less absolute average deviation percent compared with experimental data .The AAD% is 1.271 for 32 pure non polar compounds while it gives 4.439 AAD% compared with experimental data for 29 polar compounds. It is found that the First Veter method has the less deviation from experimental data among these seven method that predict the latent heat of vaporization at various temperature from normal boiling point .The AAD% is 1.344 for 18 pure non polar compounds and 446 data points on the other hand the AAD% is 3.3426 compared with experimental data for 6 polar compounds and 180 data points. This work modified kistiakowsky method two times to give accurate results with both non polar and polar compounds , These two modifications are simple and easy to use .

The first modification is the same as kistiakowsky equation except the values of constant A are different

$$\lambda_{vap\ n.b} = (A + R\ ln\ T_b)* T_b \qquad (1)$$

The AAD% obtained from this work of 34 compounds for alcohols and other polar compounds are 4.4036 and 3.38 respectively, in comparison with that of Kistiakowsky method which are 24.97 and 6.312 respectively.

The second modification of kistiakowsky method is as follows

$$\lambda_{vap\ n.b} = R.T_b (a + b*ln\ P_c + c * ln\ T_b) \qquad (2)$$

In this equation the critical pressure is included and the values of the constants a,b,c for each group were determined .

The overall AAD% obtained from this work this work for 57 compounds for non-polar compounds , alcohols and other polar compounds are 1.462 , 2.278 and 2.933 respectively , in comparison with that of Kistiakowsky method the AAD% are 2.2095 , 24.97 and 6.312 respectively predict the latent heat of vaporization at normal boiling point .

1. Introduction

The latent heat of vaporization is one of the most important thermodynamic properties of fluids, because in almost all design calculation, there is need for the values of latent heat. The analysis of phase equilibrium usually requires evaluation of change in enthalpy at saturation, thus the design of separation equipment requires enthalpy change at vaporization, which is referred to as latent heat of vaporization.

The latent heat of vaporization is the difference between the enthalpy of saturated vapor and that of the saturated liquid at the same temperature and can be explicitly defined for any system by the mathematical expression [1] :

$$\Delta H_v = \lambda_v = \Delta U_v + RT (Z_v - Z_L) \qquad (3)$$

Where

$\Delta H_v (\lambda_v)$:latent heat of vaporization

ΔU_v: internal energy of vaporization which is the work done on the vapor phase as vaporization proceeds

T: temperature of vaporization, R: constant of gases

To find the values of latent heat there are two sources of latent heat data. First, the experimental data available in literature. Second data from the accurate recommended methods for predicting the latent heat.

The pure substance can be classified according to their polarity into two categories, non-polar (normal) compounds and polar compounds.

The factors that affecting on estimation of the latent heat of vaporization are: temperature, pressure and bounding between the atoms.

The aim of this work is to evaluate the existing methods that are available in the literature for prediction of the latent heat of vaporization at various temperatures and at normal boiling point for pure compounds. Also to specify the methods which gives high accuracy with non-polar compounds and which methods give high accuracy with polar compounds . Also to indicate the limitation in each case (reduced temperature range) . Furthermore to study the possibility of modifying some simple methods to predict the latent heat of vaporization for non-polar and polar compounds with high accuracy .

3.methods

3.1 methods that predict the latent heat of vaporization at various temperatures.

3.1.1 Pitzer method

The Pitzer [1] equation use the acentric factor as a third parameter for the correlation of Z. The exact error is not known but the critical region is within the range of the correlation which was fitted to data within a very close deviation. It must be pointed out that, as with all of the three parameter corresponding states correlations, it is accurate only for "normal fluids". A "normal fluid" is nonpolar or only slightly polar. This means that it does not exhibit a dipole, quadrupole or higher moments, nor are there hydrogen bonding forces present. An example of a "normal fluid" would be hexane or carbon tetrachloride, polar compounds would be water or methyl chloride.

Pitzer used the Clausisus Clapeyron equation in combination with his vapor pressure and compressibility factor (volume) equations to develop a function (not requiring the direct calculation of either) for the heat of vaporization. The resulting equation has similar properties

to the vapor pressure, most importantly it is limited to "normal fluids".

Pitzer equation is

$$\lambda_{VAP} / T = \Delta S^{(0)} + \omega \Delta S^{(1)} \qquad (4)$$

Where $\Delta S^{(0)}$ and $\Delta S^{(1)}$ are tabulated functions of T_r. Extend of pitzer parameter by Carruth and Kobayashi [2].

3.1.2 Halm and Stiel method

The Halm and Stiel [4] method uses the acentric factor of Pitzer plus a fourth parameter, the polarity factor. This fourth parameter allowed polar forces to be described by the equation. The correlation works quite well for most polar substances, indeed much better than the three parameter correlation of Pitzer. However, the equation gave largest errors for very complex polar molecules where a simple fourth parameter is still not enough to describe the forces. Obviously the disadvantage of this method over Pitzer's is the requirement of more data, the polarity factor allowing it to predict the heat of vaporization of polar compounds.

$$\lambda_{VAP} / T = \Delta S^{(0)} + \omega \Delta S^{(1)} - \varkappa \Delta S^{(2)}) \qquad (5)$$

3.1.3 Carruth and Kobayashi

Carruth and Kobayashi [5] made an analytical representation for pitzer correlation

$$\lambda_{VAP}/RTc=7.08 (1-Tr)^{0.358}+10.95 \omega (1-Tr)^{0.65} \qquad (6)$$

3.1.4 First and Second Wagnar methods

Veter [6,7] proposed a relation similar to the one suggested by Chen. When applied to the normal boiling point:

$$\lambda_{vap} =[RT_cT_{br} (1-T_{br})^{0.38} (lnP_c -0.513 +0.5066/(P_cT^2_{br}))] / [1-T_{br} +F(1-(1-T_{br})^{0.38})lnT_{br}] \qquad (7)$$

when Tc and pc are not available Veter [8] proposed the 2nd Veter method

$$\lambda_{vap} = RT_b (A + B ln T_b + C /T_b^{1.72} / M') \qquad (8)$$

3.1.5 Lee Keslar method

Lee Kesler [9] found another form of the Pitzer equation which ,

generally predicts the vapor pressure which can mathematically be expressed as

$$\lambda_{vap} = R\, T_c\, \Delta Z_v\, (6.09648 - 1.28862\, T_r + 1.016\, T_r^7 + \omega(15.6875 - 13.4721 T_r + 2.615\, T_r^7)) \quad (9)$$

3.1.6. Antion method

Antion [10] proposed a simple modification of clapeyron equation which has been widely used over limited temperature.

$$\lambda_{vap} = R\, T_c\, \Delta Z_v\, (\; T_r\, / (A - B\, /(T+C-273.15))\,)^2 \quad (10)$$

Where A ,B and C are tabulated for a number of material From vapor pressure relations .

3.1.7 Ambrose Walton method.

This equation is two-parameter corresponding-states equation for vapor pressure. To improve accuracy, several investigators have proposed three parameter forms. The Pitzer expansion is one of the more successful equation[5] The mathematical expression of Ambrose and Walton equation for latent heat of vaporization is

$$\lambda_{vap} = R\, T_c\, \Delta Z_v = [5.97616 + 1.29874\, \tau^{0.5} * (.5\, \tau - 1.5) - .60394 \tau^{1.5}(1.5\, \tau - 2.5) - 1.06841\, \tau^4(4\tau - 5) + \omega(5.03365 + 1.11505\, \tau^{0.5})\, (0.5\, \tau - 1.5) - 5.41217 \tau^{1.5}(1.5\, \tau - 2.5) - 7.46628\, \tau^4(4\, \tau - 5)) + \omega^2(.64771 + 2.41539\; \tau^{-5})(0.5\, \tau 1.5) - 4.26979\, \tau^{1.5}).(1.5\, \tau - 0.5) + 3.25259\, \tau^4)(4\, \tau - 5))] \quad (11)$$

3.1.8 Riedel method

Riedel proposed a vapor pressure equation of the form

$$ln\, P_{vpr} = A + B/T + C\; ln\, T + DT^6 \quad (12)$$

The T^6 term allows description of the inflection point of the vapor pressure curve .

To determine the constants in Eq. (13), Riedel defined a parameter :

$$\alpha = d(lnP)/\, d(lnT) \quad (13)$$

From a study of experimental vapor pressure data, Plank and Riedel [11] showed

that $d(lnP)/\, d(lnT) = 0$ at $T_r = 0$

Using Eq. (12) as a constraint on Eq. (13)plank an Riedel found that

$$\lambda vap = R\, T_c\, Z_v\, [\, B + + C + Tr + 6D + Tr7\,] \quad (14)$$

where

$A+ = -35Q, B+ = -36Q, C+ = 42Q + \alpha_C,\; D+ = - Q,\; Q = K(3.758 - C)$
where α_C is at the critical point

$$\alpha_C = (3.789K\, \psi_b + ln\, ((P_c\, /1.01325)) / K\, \psi_b - ln\, T_{br} \quad (15)$$
$$b = - 35 + 36\, /\, T_{br} + 42\; ln\, T_{br} - T_{br}^6 \quad (16)$$

The optimized K values are linked to a well-known property of the compound through generalized correlations, which are valid for all the compounds that belong to the same family.

Nonpolar compounds	K = 0.066 + 0.0027H	**(17a)**
Acids	K = -0.120 + 0.025H	**(17b)**
Alcohols	K = 0.373 - 0.030H	**(17c)**
glycols	K = 0.106 - 0.0064H	(**17d**)
Other polar compounds	K = -0.008 + 0.14	**(17e)**

Where

$$H = T_b\; ln(P_c/1.01325)/\; 1 - T_{br} \quad (18)$$

3.2 Methods of predicting the latent heat of vaporization at normal boiling point of pure compounds.

3.2.1 Riedel method

Riedel modified eq (24) slightly and proposed that

$$\lambda_{vap(n.b)} = 1.093\, R\, T_c\, T_{br}\, (lnP_c - 1.013)\, /(0.93 - T_{br}) \quad (19)$$

3.2.2 Chen method

Chen [15] used a similar expression proposed by Pitzer to correlate vapor pressures so that the acentric factor is eliminated. He obtained a relation between dHv ,Pvp and Tr , when applied at the normal boiling point.

$$\lambda_{vap\, (n.b\,)} = (3.978 T_{br} - 13.9758 + 1.555\, lnP_c\,)/(\, 1.07 - T_{br}) \quad (20)$$

4.2.3 First Veter method

Veter [6,7] proposed a relation similar to the one suggested by Chen. When applied to the normal boiling point:

$$\lambda_{vap(n.b)} = (RT_c T_{br}(1-T_{br})^{0.38} (lnP_c -0.513 +0.5066/(P_c T^2_{br}))) / (1-T_{br} +F(1-(1-T_{br})^{0.38})lnT_{br}) \qquad (21)$$

F is 1.05 for alcohols and dimerizing compounds such as SO3 , NO, and NO2.. For all other compounds investigated by Veter, F is 1.0.

3.2.4 Fishten method

Fishtine [12] modified Kistiakowsky relation and expressed heat of vaporization at normal boiling point as

$$\lambda_{vap(n.b)} = (4.7 T_c (1.0 - P_{rb})^{0.69} log P_{rb})/(1- 1/T_{rb}) \qquad (22)$$

3.2.5 Calypyron method

when the clapeyron equation is used to calculate ψ regardless T_r, ψ is equal to

$$\psi(T_r) = \psi(T_b) = T_b (ln (P_c/1.01325)/(1 - T_{br}) \qquad (23)$$

$$\lambda_{vap(n.b)} = R T_c \Delta Z_{vb} \ T_{br} \ ln (P_c/1.01325) /1 - T_{br} \qquad (24)$$

3.2.6 Second Veter method

when T_c and p_c are not available Veter [8] proposed

$$\lambda_{vap} = RTb (A + B ln T_b + C /T_b 1.72 / M') \qquad (25)$$

Where A, B and C are given in table 1.a, M' is a fictitious molecular weight that is equal to the true molecular weight for most compounds. But for fluids that contain halogens or phosphorus, the molecular weight contributions for these atoms are those shown in table 1.b.

Table 1.a The constants of second Veter method

Groups	A	B	C
Hydrocarbons	3.298	1.015	0.00352
Alcohols	13.173	4.359	0.00151
Esters	4.814	0.890	0.00374
Other polar compounds	4.542	0.840	0.00352

Table 1.b The molecular weight contributions for second Veter method

Atom	Contribution
F	1
Cl	19.6
Br	60
I	60
P	24

3.2.7 Kistiakowsky method (modified)

The Kistiakowsky [13] rule is another simple equation that can be used to estimate latent heat of vaporization at normal boiling point

$$\lambda_{vap(n.b)} = (36.1+R \ ln \ Tb) \ Tb \qquad (26)$$

First modification

In this work the above simple equation was modified as follows

$$\lambda_{vap} = (A+ R \ ln \ T_b) \ T_b \qquad (27)$$

where A is constant T_b boiling point temperature in degrees K, R is gas constant equals 8.314 J/mole.K .This equation was applied to more than 60 compounds and it was found that it is more convenient to classify the compounds to three groups each with its own constants . These groups are: non polar, alcohol and other polar compounds as shown in table 2.

Table 2 The values of first modification's constant of each group

Groups	Value of A
non polar component	36.1
alcohol	56.44
other polar component	41.36

Second modification

Both eq(22,23)are proposed when the critical pressure was not available. In this work, the above simple equation was modified to include the critical pressure of compounds as follows

$$\lambda_{vap} = R.Tb (a + bln P_c +c \ ln \ T_b) \qquad (28)$$

Where a,b,c are constants , T_b boiling point temperature in degrees K, P_c is critical pressure in bar and R is gas constant (8.314 J/mole.k)This equation was applied to

more than 64 compounds and it was found that it is more convenient to classify the compounds in to three groups each with it's own constants . These groups are non-polar compounds, alcohol and other polar compounds as shown in table 3.

Table 3. The values of second modifications' constants of each group.

Groups	a	b	c
Non polar	1.18306	0.49459	1.2634
alcohol	32.8115	0.22592	-3.48002
Other polar	6.6869	-0.72627	1.157612

3.3 Methods of predicting the latent heat of vaporization at any temperatures from those at normal boiling point of pure compounds

Latent heat of vaporization at any temperatures can be predicted from those at normal boiling point by using Watson eq

$$dHv = dHv_{ref} \ ((1-T_r)/(1-T_{r\,ref}))^n$$

by using one data point as a reference. Several authors have studied this relationship most agreeing that the power n, while it does vary somewhat, should be 0.38. Thods [45] found that for 44 substances the average value of n to be   0.378.
where n= .38

The expected errors will be least between the reference point and the critical point, and increasing at lower temperatures

4. results and discussion

4.1 results and discussion   the latent heat of vaporization   at various temperatures

4.1.1 Pitzer method

The overall absolute average deviation percent of Pitzer method for 24 compounds and 626 data point is 1.956 compared with experimental data . This method is easy to use and can be applied to all compounds and the results indicate that it is one   of the best methods to predict the latent heat of vaporization of pure non polar compounds.The overall absolute average deviation percent for 18 non polar compounds and 446 data point is 1.55% and .The overall absolute average deviation percent for 6 polar compounds and 180 data point is 3.16.

Thus this method can be considered as an excellent method for non-polar compounds but it is not so accurate for polar compounds .
The results[3] indicate that this method can be applied at reduced temperature range of 0.3 to just below the critical region for non-polar compounds while the reduced temperature range of 0.45 until critical region for polar compounds .

4.1.2 Halm and Stiel method

The overall absolute average deviation percent of Halm and Stiel method for 24 compounds and 626   data point is 1.876 compared with experimental data. The results indicate that it is the best method among the nine methods. This method can predict the latent heat of vaporization for both non-polar and polar pure compounds with high accuracy. It can also be applied to all compounds. Since the parameters needed are available in literature or can be calculated easily. The overall absolute average deviation percent for eighteen non polar compounds and 446 data points is 1.55 while the absolute average deviation percent for six polar compounds and 180 data point is 2.845 .

It is to be noted that it is the only method that deals especially with polar compounds by introducing what is known as polarity factor , The results also indicate that this method gives excellent results (least deviations from experimental data) at reduced temperature range of 0.3 to just below 0.99 .

4.1.3 Carruth and Kobayashi

The overall absolute average deviation percent of Carruth and Kobayashi for 24 compounds and 626 data point is 2.11 compared with experimental data .This method is easy to use and can be applied to all compounds.The accuracy of this method for predicting the latent heat of vaporization of non-polar pure compounds is as good as Halm Stiel and Pitzer method. The overall absolute average deviation percent for 18 non polar compounds and 446 data point is 1.52 .However it is not so accurate for polar pure compounds whereas the overall absolute average deviation percent for 6 polar compounds and 180 data point is 3.52. The results also indicate that Carruth and Kobayashi method works at low reduced

temperature up to reduced temperature of 0.97 where in the region from 0.97 to 1.0 has relatively high deviation from experimental latent heat of vaporization data .

4.1.4 First and Second Wagnar methods

The overall absolute average deviation percent for 7 pure compounds and 207 data points are 2.24 and 1.102 for first and second Wagnar methods respectively compared with experimental data .The results indicate that the second wagnar method is better than the first Wagnar method for prediction of the latent heat of vaporization of pure non polar and polar compounds. The disadvantage of these methods is the fact that they have a special constants for each compounds called Wagnar constants and these constants are not available in literature for most compounds . In case the parameters are available this equation shows high accuracy for temperature range from low temperature to near critical temperature [9].

4.1.5 Lee Keslar method

The overall absolute average deviation percent of Lee Keslar method for 14 compounds and 417 data point is 1.26 compared with experimental data .The disadvantage of this method is that it cannot be applied to all compounds thus it cannot be considered as one of the very successful methods . The results indicate that Lee Keslar method works even at low reduced temperature for non-polar compounds while in polar compounds it works from reduced temperature of o.5 to just below 0.99.

4.1.6. Antion method

The overall absolute average deviation percent of Antion method for 14 compounds and 417 data point is 4.6474 compared with experimental data .The results indicate that this method is not very successful method to predict the latent heat of vaporization of pure non polar or polar compounds .

4.1.7 Ambrose Walton method.

This equation is two-parameter corresponding-states The overall absolute average deviation percent of Ambrose Walton method for 14 compounds and 417 data point is 1.363 compared with experimental data. However it has good results to predict the latent heat of vaporization for pure non polar compounds .However it has some

limitations since it is not easy to use and its parameters are not available in literature for all compounds.

4.1.8 Riedel method

The overall absolute average deviation percent of Riedel method for 14 compounds and 417 data point **is** 1.88 compared with experimental data. The results indicate that it is good method to predict the latent heat of vaporization for pure non-polar compounds. It cannot be considered as one of the successful methods because it is difficult to use and cannot be applied to all compounds.

4.2 results and discussion of Methods of predicting the latent heat of vaporization at normal boiling point .

4.2.1 Riedel method

The overall absolute deviation percent of Riedel method for 61 compounds is 2.767 compared with experimental data. Riedel method is easy to use and can be applied to all compounds. The results indicate that Riedel method is the best method among seven methods to predict the latent heat of vaporization at normal boiling point for pure compounds especially for non-polar pure compounds whereas the overall absolute deviation percent of 32 non polar compounds is 1.271.

4.2.2 Chen method

The overall absolute deviation percent of Chen method for 61 compounds is 2.818 compared with experimental data. This method is easy to use and can be applied to all compounds. The results indicate that Chen method can be considered as one of the best methods to predict the latent heat of vaporization at normal boiling point for pure non polar compounds. The overall absolute deviation percent of 32 non polar compounds is 1.255 .However the overall absolute deviation percent of 29 polar compounds is 4.471 .

4.2.3 First Veter method

The overall absolute deviation percent of 61 compounds using this method is 3.255 compared with experimental data. The overall absolute deviation percent of 32 non-polar compounds is 1.496 as shown in table 3.5 and the overall absolute deviation percent of 29 polar compounds is 5.059. Thus, the First Veter method has high accuracy

in for non-polar compounds and also it can be applied for all compounds but it is not so accurate for polar compounds.

4.2.4 Fishten method

The overall absolute deviation percent of Fishten method of 61 compounds is 3.27 compared with experimental data . The overall absolute deviation percent of 32 non-polar compounds is 2.647, while the overall absolute deviation percent of 29 polar compounds is 3.905. The results indicate that Fishten method is the best method among the seven methods to predict the latent heat of vaporization at normal boiling point for polar compounds also it can be applied for all compounds.

4.2.5 Calypyron method

The overall absolute deviation percent 61 compounds using this method is 3.799 compared with experimental data. The overall absolute deviation percent of 32 non-polar compounds is 2.327 while the overall absolute deviation percent of 29 polar compounds is 5.316. These results indicate that the Calypyron method has very good results for non-polar compounds but it does not give good results when dealing with polar compounds. The disadvantage of this method that it cannot be applied to all compounds.

4.2.6 Second Veter method

The overall absolute deviation percent of 61 compounds using this method is 4.75 compared with experimental data. The overall absolute deviation percent of 32 non polar pure compounds is 4.271.The overall absolute average deviation percent of 29 polar pure compounds is 5.456.These results indicate that second Veter method is not so accurate for prediction of the latent heat of vaporization for both non polar and polar compounds .

4.2.7 Kistiakowsky method (modified)

The Kistiakowsky [14] rule is another simple equation that can be used to estimate latent heat of vaporization at normal boiling point

$$\lambda_{vap(n.b)} = (36.1 + R \ln T_b) \, T_b \qquad \qquad \textbf{(26)}$$

The overall absolute deviation percent of 61 compounds using this method is 8.375 compared with experimental data. The results indicate that it is not successful method to predict the latent heat of vaporization at normal boiling point. This high deviation from experimental data is due to the fact that this method does not work with polar pure compounds whereas the overall absolute deviation percent of 32 non polar compounds is 3.379 and the overall absolute deviation percent of 29 polar compounds is 13.66. These results also indicate that it is relatively good method to predict the latent heat of vaporization of pure non polar compounds. The method is simple method and can be applied to all compounds .

First modification

The overall absolute average deviation percent obtained for this work of 34 compounds for alcohols(including water) and other polar compounds are 4.4036 and 3.38 respectively, in comparison with that of Kistiakowsky method which are 24.97 and 6.312 respectively.

Second modification

The overall absolute average deviation percent of non-polar compounds for kistiakowsky equation is 2.2095 while the overall absolute deviation percent of non-polar compounds for this work is 1.4620 .For alcohol the overall absolute deviation percent for Kistiakowsky equation is 19.14 and the overall absolute deviation percent of this work is 2.278 , The overall absolute deviation percent[15] for other polar compounds of Kistiakowsky is 6.206 and the overall absolute deviation percent of this work is 2.933. The overall absolute deviation percent of three groups using Kistiakowsky equation is 8.608 and the overall absolute deviation percent of three groups of this work is 2.106 this indicates that Kistiakowsky equation does not work with polar compounds at normal boiling point ,however Kistiakowsky equation works for non-polar compounds but with relatively high deviation from experimental data at normal boiling point, and this work gives less deviations for all the three classes compounds from experimental data especially when dealing with polar compounds .

4.3 methods of predicting the latent heat of vaporization at any temperatures from those at normal boiling point

4.3.1 Riedel method

The overall absolute average deviation percent at various temperatures from those of 24 compounds and 626 data point is 1.98 compared with experimental data .Riedel method as mentioned before is easy to use and can be applied to all compounds . The results indicate that Riedel method has excellent agreement with experimental data for non-polar compounds. The overall absolute average percent deviation for 18 non-polar compounds and 446 data points is 1.38. However, this method is not so accurate for polar compounds whereas the overall absolute average percent deviation for six polar compounds and 180 data point is 3.81 .Thus Riedel method can be considered as the best method to predict the latent heat of vaporization of non-polar compounds among the seven methods. The results also indicate that this method works safely near the critical region but it is not so safe at reduced temperature below 0.3 specially for polar compounds.

4.3.2 Fishten method

The overall absolute average deviation percent of Fishten method for 23 compounds and 625 data point is 2.813 compared with experimental data. The results indicate that this method is very good to predict the latent heat of vaporization of pure non polar and polar compounds. This method as mentioned before can be applied for almost all compounds. The overall absolute average deviation percent for 17 non polar compounds and 430 data points is 2.11 . The overall absolute average deviation percent for 6 polar compounds and 180 data point is 3.463. The results also indicate that Fishten method works accurately for non-polar compounds at reduced temperatures ranges from 0.25 to just below 0.99 while it works accurately for polar compounds at reduced temperatures range of 0.3 to just below 0.97 .

4.3.3 Chen method

*the overall absolute average deviation percent of Chen method for 24 compounds and 626 data point **is** 2.138 compared with experimental data. This method is easy to use as mentioned before and can be applied to all*

compounds. The results indicate that it is very good method to predict the latent heat of vaporization of pure compounds. The overall absolute average deviation percent of 18 non polar compounds and 446 data point is 1.422 while the overall absolute average deviation percent of 6 polar compounds and 180 data point is 4.07. Thus, this method is a very successful method to predict the latent heat of vaporization of pure non-polar compounds.

4.3.4 First Veter method

The overall absolute average deviation percent of First Veter method for 24 compounds and 626 data point is 1.84 compared with experimental data. Thus it is one of the best method to predict the latent heat of vaporization for pure non polar and polar compounds . The overall absolute average deviation percent for 18 non polar compounds and 446 data point is 1.34 while the overall absolute average deviation percent for 6 polar compounds and 180 data point is 3.34%. These results indicate that this method is very accurate with polar compounds compares with other methods. First veter method works at wide range of reduced temperatures even when nearby the critical region for non-polar compounds. While for polar compounds the deviation comparatively increases when reduced temperature becomes higher the .98. Thus it does not give excellent prediction of latent heat of vaporization over reduce temperature of 0.9 for polar compounds.

4.3.5 Second Veter method

The overall absolute average deviation of Second Veter method for 24 compounds and 626 data point is 3.49 compared with experimental data. The results indicate that it is good method to predict the latent heat of vaporization of pure non polar and polar compounds .The overall absolute average deviation percent of 18 non polar compounds and 446 data point is 2.58 while the overall absolute average deviation percent of 6 polar compounds and 180 data point is 5.03 .These results indicate that the Second Veter method is very successful method to predict the latent heat of vaporization of pure non polar compounds while it is not so successful to predict the latent heat of vaporization of polar compounds . The results also indicate that this method works rather good for reduced temperature ranges from 0.4 to just below 0.96.

4.3.6 Calpeyron method

The overall absolute average deviation percent of Calpeyron method for 23 compounds and 609 data point is 3.08 compared with experimental data .The results indicate that it is good method to predict the latent heat of vaporization .The overall absolute average deviation percent for 18 non polar compounds and 446 data point is 2.45 while the overall absolute average deviation percent for 5 polar compounds and 163 data point is 5.37 .This indicates that the Calpeyron method is very good method to predict the latent heat of vaporization for non-polar compounds while it is not so successful to predict the latent heat of vaporization of polar pure compounds. The results indicate that Calpeyron method works at reduced temperature range of 0.25 to 1.0 .

4.3.7 Kistiakowsky method

The overall absolute average deviation of Kistiakowsky method for 24 compounds and 626 data point is 6.528 compared with experimental data. The results indicate that the Kistiakowsky method is not so successful method to predict the latent heat of vaporization of pure compounds . The overall absolute average deviation percent of 18 non polar compounds and 446 data point is 2.7957 while the overall absolute average deviation percent of 6 polar compounds and 180 data point is 17.724. The results indicate that the Kistiakowsky method is very good to predict the latent heat of vaporization of pure non-polar compounds and can be applied for all non-polar compounds. The results indicate that this method can be used safely at low temperature and near the critical region.

5. Conclusions

1. The latent heat of vaporization can be predicted from vapor pressure data , law of corresponding states and empirical methods .The first and second methods predict the latent heat of vaporization at any temperature while the third method predicts the latent heat of vaporization at normal boiling point.

2. There are at least nine methods available in literature for prediction of latent heat of vaporization at any temperature using either vapor pressure data or the law of corresponding states . These methods are Halm Stiel ,Pitzer ,Carruth Kobayashi , Wagnar 1, Wagnar2, Lee-Keslar, Antion ,Ambrose Walton and Riedel method .All of them are evaluated in this work .Among these methods the Pitzer ,Halm stiel and Carruth Kobayashi methods are the most accurate for non-polar compounds .The AAD% for 18 non polar compounds and 446 data point are 1.552,1.552.and 1.52 respectively .

3. There are also at least seven methods available in literature for prediction of latent heat of vaporization at normal boiling point .These methods are Riedel ,Fishtine , Chen , Veter 1,Veter 2, Calpeyron and Kistiakowsky method. All of them are evaluated in this work . Among these method the Riedel and Chen methods are the most accurate for non-polar compounds. The AAD% for 32 non polar compounds are 1.27 and 1.255 respectively and the AAD% for 29 non polar compounds are 4.439 and 4.471 respectively .On the other hand Fishten method is most accurate of these methods for polar compounds which gives 3.905 %for 29 polar compounds .

These methods can be applied at various temperatures by using Watson equation .It is found that the First Veter method has less deviation from experimental data .The AAD% is 1.344 compared with experimental data for 18 pure non polar compounds and 446 data points .On the other hand it gives 3.3426 AAD% compared with experimental data for 6 polar compounds and 180 data points.

4. Two empirical modifications have been done on Kistiakowsky method in this work to predict the latent heat of vaporization at normal boiling point .These two modifications are simple and easy to use .In both modifications the compounds are classified into three groups :non polar ,alcohols(including water) and other polar compounds and the values of constants are given for each group.

The first modification is the same as Kistiakowsky equation except the values of constant A are different

$$\lambda_{vap\ n.b} = (A + R\ ln\ T_b)\ T_b$$

The overall absolute average deviation percent obtained for this work of 34 compounds for alcohols(including water) and other polar compounds are 4.4036 and 3.38 respectively, in comparison with that of

Kistiakowsky method which are 24.97 and 6.312 respectively.

5. The second modification of Kistiakowsky method is as follows

$$\lambda_{vap\ n.b} = R.T_b\ (a + b\ ln\ P_c + c\ ln\ T_b\ )$$

In this equation the critical pressure is included and the values of the constants a,b,c are tabulated.

The overall absolute average deviation percent obtained in this work for 57 compounds for non-polar compounds , alcohols and other polar compounds are 1.462 , 2.278 and 2.933 respectively , in comparison with that of Kistiakowsky method which are 2.2095 , 24.97 and 6.312 respectively.

It is to be noted that this work has the least deviation from experimental data for all methods that predict the latent heat of vaporization at normal boiling point for pure polar compounds. This work also applied at various temperatures by using Watson equation .

5. Acknowledgement

6. Nomenclature

A,B,C	Antion constant
a,b,c,d	Wagnar constant
A^+,B^+,C^+,D^+	Riedel constant of equation of equation (3-9)
dHv(λ_{vap})	latent heat of vaporization (J/mole)
F	Veter constant of equation (3-15)
K	Riedel constant of equation (2-33)
m	Grain Lyman constant
Mwt	Molecular weight
$Mwt^{/}$	Contribution molecular weight
n	Watson constant
P	Pressure (bar)
P_{br}	Reduced temperature at normal boiling point
P_c	Critical pressure (bar)
P_r	Reduced pressure

P_{vp}	Vapor pressure (bar)
R	Universal gas constant (J/mole.K)
$\Delta S^0 , \Delta S^1 , \Delta S^2$	Pitzer s' parameters
T	Temperature (K)
T_b	Normal boiling temperature (K)
T_{br}	Reduced temperature at normal boiling point(K)
T_c	Critical temperature (K)
T_r	Reduced temperature
ΔU_v	Internal energy of vaporization
ω	Acentric factor
χ	Polarity factor
Z_c	Critical compressibility factor
ΔZ	Compressibility factor of vaporization
$\lambda_{vap\ n.b}$	Latent heat of vaporization at normal boiling point(J/mole).
ĭ	$1-T_r$
α	Riedel factor
α_c	Riedel factor at critical properties

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