SHORT COMMUNICATION

A new vapor pressure equation for pure substances

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Abstract-A new simple equation for prediction of vapor pressure of pure substances is proposed. The equation which has the Clausius-Clapeyron (C-C) equation form consists of three parameters: critical temperature, critical pressure and normal boiling point. Experimental data for organic and inorganic substances have been used to calculate equation parameters in the boiling point ranges from 169.45 to 457.55 K and critical temperature ranges from 282.75 to 699.15 K. Comparison of proposed equation estimation results with experimental data shows that the new equation has minor average error. The new equation is also 68 percent more accurate than the C-C equation

Key words: Vapor Pressure, Clausius-Clapeyron Equation, M-Z Equation

INTRODUCTION

One of the most important physical properties of pure liquids used by engineers in the oil and gas industries is vapor pressure [1-5]. To perform thermodynamic calculations, basic properties of the fluid or fluid mixtures must be known or be able to be estimated. Such properties include liquid and vapor densities, molecular weight, normal boiling point, vapor pressure, critical temperature, critical pressure, critical volume or compressibility factor and acentric factor. Otherwise, other estimations should be used [6]. Vapor pressure is an important thermo-physical property in numerous chemical processes and product design applications [7]. Knowledge of pure-fluid vapor pressure is also essential to understanding fluid phase behavior and to perform multiphase equilibrium calculations of multi-component systems [8-10]. Traditionally, vapor pressure has been determined experimentally by techniques of varying complexities, and experimental measurements are still needed when dealing with challenging fluids. However, experimental determination of vapor pressures noting increasing number of chemicals requires significant time and cost investments. The problem becomes serious when dealing with hazardous chemicals [11].

Many correlations for estimating vapor pressures have been used to complement existing experimental measurements [12].

A review of vapor pressure equations (VPEs) in the literature indicates that most VPEs have their origin in the Clausius-Clapeyron equation:

$$\frac{d(\ln p)}{d(1/T)} = -\frac{\Delta H_{IV}}{R(\Delta Z_{IV})} \tag{1}$$

Where p is the pressure, T the temperature, and R is the gas constant. ΔH_{lv} and ΔZ_{lv} are changes in enthalpy and compressibility factor associated with vaporization. Integration of the Clausius-Clapeyron equation leads to most of the widely used vapor pressure correlations. However, this integration requires some assumptions regarding temperature dependence of the $\Delta H_{lv}/\Delta Z_{lv}$ ratio. Assuming that $\Delta H_{lv}/\Delta Z_{lv}$ is constant leads to the simplest vapor pressure equation:

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$$\ln p = A + \frac{B}{T} \tag{2}$$

Where A is an integration constant and B=$-\Delta H_{lv}/(R(\Delta Z_{lv}))$. Both A and B are determined from experimental vapor pressure data. This correlation is precise in representing vapor pressures over small temperature intervals; however, it fails to estimate accurately when used to represent vapor pressure data for the entire saturation range. Eq. (2) can be written in critical temperature and pressure as below:

$$\ln p_r = A + \frac{B}{T_r} \tag{3}$$

Several modifications of the equation have been proposed. In one modification in order to increase precision of VPEs, polynomial-type models with varying temperature exponents have been proposed [13] (Wagner equation):

$$\ln p_r = \frac{A(1-T_r) + B(1-T_r)^{1.5} + C(1-T_r)^3 + D(1-T_r)^6}{T_r} \tag{4}$$

Where T_r and p_r are the reduced temperature and pressure, respectively. The model parameters A-D are empirical and experimental data are required to determine their values. Mejbri-Bellagi represent the following VPE [14]:

$$\ln p_r = \beta_1(\tau - \exp(1-\tau)) + \beta_2(\tau^{\beta_3} - \exp(1-\tau)) \tag{5}$$

Where $\tau = 1/T_r$.

Numerous empirical vapor-pressure equations have been published; the best known VPEs are those of Clausius, Antoine, Frost-Kalkwarf, Cox, Gomez-Thodos, Lee-Kesler, Ambrose-Walton and Riedel [15,16].

THE NEW GENERALIZED EQUATION

The new generalized equation, Mohammadzadeh-Zahedi (M-Z) equation, has the following form:

$$\frac{d\left(\ln P_v^{\frac{ln(T_C/T_b)}{ln P_C}}\right)}{d(\log T)} = -\frac{\Delta H_{IV}}{R(\Delta Z_{IV})} \tag{6}$$

This equation is the simplest equation the same as the C-C equation, which can be used to calculate the vapor pressure of organic and inorganic substances. It has been assumed that the new equation be linear with temperature. To have all ranges in graphs, the logarithm of pressure has been selected for the x-axis. For the same reason, the pressure unit in y-coordinate has been set to be bar. To guarantee linear form of the equation, the vapor pressure has been assumed to have power n. So P^n-log(T) and we will have the following form for the M-Z equation as:

$$P_v^n = A\log T + B \tag{7}$$

Temperature varies between boiling pint and critical point as illustrated in Fig. 1.

Value of n is necessary for calculations; n is assumed to have the following form:

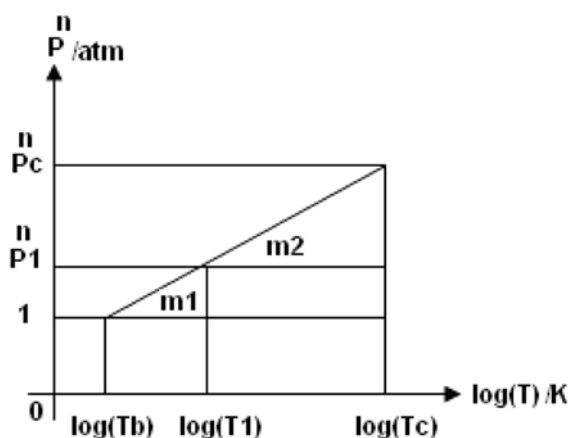$$n = \frac{\ln(T_C/T_b)}{\ln P_C} \tag{8}$$

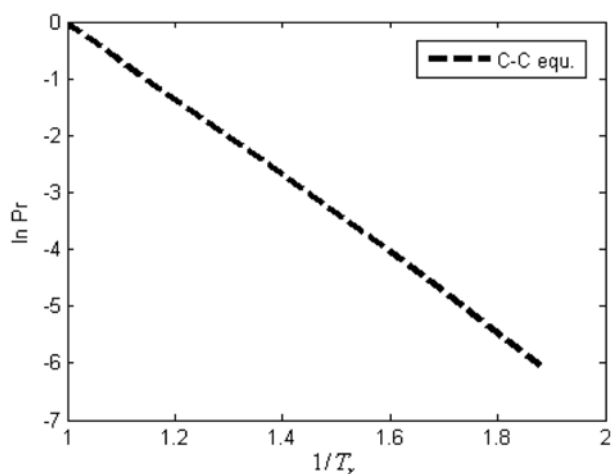Fig. 1. Schematic of variation of pressure with temperature to obtain the M-Z equation.

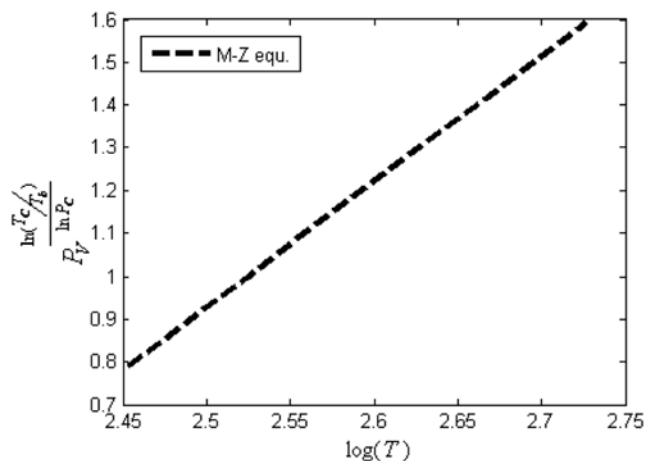Fig. 2. Variation of vapor pressure for chloroform (C-C equation).

Fig. 3. Variation of vapor pressure for chloroform (M-Z equation).

Table 1. Main characteristics of the considered substances

Compounds	T_b/K	T_c/K	P_c/MPa	T_m/K	N
1,3 Butadiene	268.65	434.95	4.3164	226.35	11
Butryric acid	436.65	628.15	5.2689	381.15	12
Ammonia	239.55	405.55	11.298	204.75	13
Cyclohexane	353.85	553.05	4.0327	298.65	10
Diethyl amine	328.65	496.45	3.7085	279.15	10
DME	249.45	400.05	5.2689	210.45	12
Ethane	184.55	305.45	4.8839	153.85	11
Ethanol	351.44	513.92	6.2493	308.05	13
Ethyl mercaptane	308.15	498.65	5.4918	260.15	12
Ethylene	169.45	282.75	5.1372	141.35	12
Hydrogen chloride	188.85	324.55	8.2681	159.15	13
Acetone	329.65	508.15	4.7623	280.85	11
Methanol	337.85	513.15	7.9743	294.35	13
Methyl acetate	330.95	506.85	4.6913	282.55	11
n-Butane	272.65	425.95	3.6477	228.95	10
n-Heptane	371.55	539.95	2.7256	314.95	9
n-Hexane	341.87	507.49	3.0270	315.74	54
n-Octane	398.75	569.35	2.5027	338.85	9
n-Propane	231.05	369.95	4.2557	193.55	11
Phenol	455.05	692.15	6.1302	394.55	12
n-Pentane	309.21	469.70	3.3674	260.55	45
2-Propanol	355.65	508.15	5.3702	312.65	12
Propylamine	321.65	496.95	4.7420	273.65	11
R121[a]	320.75	487.25	3.4147	271.45	10
Sulfur dioxide	263.15	430.35	7.8730	226.45	13
Toluene	383.75	593.75	4.2151	325.05	11
Aniline	457.55	699.15	5.3094	393.05	12
Benzene	353.25	563.65	5.0764	299.25	12
Chlorobenzene	405.35	632.35	4.5191	343.85	11
Ethyl bromide	311.55	503.95	6.2315	277.65	12
n-Propylformate	354.45	537.95	4.0023	302.65	10
Chlorotriflouromethane	191.95	326.15	4.0834	161.45	11
n-Butyl alcohol	390.65	560.15	4.9041	343.25	11
Chlorine	239.35	417.15	7.6987	201.45	13
Chloroform	334.45	533.15	5.5627	283.55	12
Water	373.15	647.30	22.050	324.75	100

[a]1,1,2-Trichloro-1,2,2-trifluoro ethane

By replacing this value in Eq. (7), the following form is obtained for the M-Z equation:

$$P_V^{\frac{ln(T_C/T_b)}{ln\,P_C}} = [A\,log\,T + B] \qquad \text{(M-Z) Equation} \qquad (9)$$

In the M-Z equation A and B are slope and intercept of Eq. (7) which can be obtained from boiling point and critical point coordinates as (Fig. 1):

$$A = \frac{P_C^{\frac{ln(T_C/T_b)}{ln\,P_C}} - 1}{log\left(\frac{T_C}{T_b}\right)} \qquad (10)$$

$$B = 1 - A\,log(T_b) \qquad (11)$$

1. Method for Obtaining M-Z Equation

The routines in obtaining the M-Z equation have been implemented by programming in Matlab 7. We need two points to fit experimental data, calculate the slope and intercept of the new equation, where determined points are (boiling point temperature-atmospheric pressure) and (critical temperature-critical pressure). In the new equation, A is slope and B intercept, where slope and intercept have been calculated with (8) and (9) relations. In fact, the new equation had been a correction of Clausius-Clapeyron equation. Figs. 1 and 2 show the variation of vapor pressure curves with temperature for C-C and M-Z equations.

Table 2. Coefficients and percent errors of C-C and M-Z equations for the considered substances

Compounds	Coefficients Eq. (7)		Coefficients Eq. (3)		Error %	
	A	B	B	A	Eq. (7)	Eq. (3)
1,3 Butadiene	2.9582	−6.1816	−6.2084	6.2353	3.1681	4.4781
Butryric acid	2.7770	−6.3316	−9.1682	9.1865	2.0951	2.6113
Ammonia	3.1049	−6.3879	−6.8839	6.9112	1.5427	2.0234
Cyclohexane	2.9026	−6.3983	−6.6515	6.6680	0.8496	2.7098
Diethyl amine	2.8501	−6.1730	−7.1875	7.2139	1.9359	3.0704
DME	2.8498	−5.8309	−6.5998	6.6107	0.9273	2.0580
Ethane	2.9937	−5.7841	−5.9538	5.9588	1.2196	1.8856
Ethanol	2.8012	−6.1315	−9.0591	9.0645	4.3117	4.6047
Ethyl Mercaptane	2.9574	−6.3604	−6.5170	6.5213	0.5212	2.0780
Ethylene	3.0070	−5.7027	−5.9314	5.9512	1.4488	1.9279
Hydrogen chloride	2.8526	−5.4928	−6.1421	6.1453	1.3587	1.6768
Acetone	2.8812	−6.2549	−7.2744	7.3213	2.3504	3.4431
Methanol	2.8585	−6.2283	−8.5795	8.6194	3.0112	3.4632
Methyl acetate	2.8712	−6.2346	−7.3203	7.3388	1.5056	3.1020
n-Butane	2.9222	−6.1167	−6.4994	6.5416	2.2153	3.3984
n-Heptane	2.7920	−6.1754	−7.3806	7.3887	1.9062	2.3821
n-Hexane	2.8237	−6.1549	−7.0110	7.0120	0.6613	0.8932
n-Octane	2.7660	−6.1935	−7.6331	7.6493	1.8293	2.7252
n-Propane	2.9406	−5.9507	−6.2782	6.2881	1.1066	2.6636
Phenol	2.8606	−6.6038	−8.0620	8.1272	5.2969	5.5032
n-Pentane	2.8586	−6.1187	−6.7845	6.7896	0.6349	1.5055
2-Propanol	2.7670	−6.0586	−9.5020	9.5414	4.1649	4.4554
Propylamine	2.8847	−6.2330	−7.1543	7.1749	1.6226	2.7636
R121	2.8587	−6.1644	−6.9600	7.0077	3.2358	3.5369
Sulfur dioxide	2.9744	−6.1986	−7.0284	7.0880	4.3577	4.9103
Toluene	3.0196	−6.8028	−6.9154	6.9395	1.1848	3.0869
Aniline	2.8677	−6.6293	−7.6684	7.7241	4.1796	4.6746
Benzene	2.9351	−6.4789	−6.6663	6.6868	1.3783	2.9382
Chlorobenzene	2.8897	−6.5619	−6.8890	6.9040	1.1074	2.4799
Ethyl bromide	2.9568	−6.3729	−6.6663	6.6868	4.7694	6.9192
n-Propylformate	2.8573	−6.2848	−7.2823	7.3233	3.1684	4.3052
Chlorotriflouromethane	3.0367	−5.9334	−5.5306	5.6140	7.3058	8.4744
n-Butyl alcohol	2.7722	−6.1849	−9.2013	9.2301	4.3673	4.7939
Chlorine	3.0790	−6.3251	−5.9210	5.9570	1.7610	2.4673
Chloroform	2.9336	−6.4054	−6.7973	6.7996	0.6784	2.1845
Water	3.0712	−6.8987	−7.3506	7.3725	2.1499	2.4335
Total percent average error					**2.3702**	**3.2952**

Fig. 2 shows that the C-C equation has linear form with negative slope and Fig. 3 indicates that the new equation has linear form with positive slope.

DATA BASE

Table 1 represents experimental data sets for building the M-Z equation. T_m in this table stands for the lower limit of the temperature range; the upper limit is always the critical temperature, N is the number of data points used for determining of the adjustable parameters. The saturation properties of the rest of the substances are looked up from the NIST data bank and Perry's Chemical Engineers' Handbook [17,18].

RESULTS AND DISCUSSION

The coefficients A and B of Eqs. (7) and (3) are tabulated in Table 2. The vapor pressure data are fitted with Eq. (7) by using the Matlab version of 7, a fitting program based on the linear equation method. The coefficients A and B of model (7) are given in Table 2, where coefficients are calculated by using the relations (8) and (9). For coefficients calculation of model (3), Matlab programming (unit pressure in model (3) is Mpa) has been implemented for fittings. To evaluate the accuracy of the proposed model and previous model, the following percent error criterion was used.

$$\text{error } \% = \frac{100}{N} \times \sum_{j=1}^{N} \left| \frac{P_{exp} - P_{cal}}{P_{exp}} \right|_j \tag{12}$$

The M-Z equation is valid for both organic and inorganic substances in the boiling point range of $169.45 \leq T_b \leq 457.55$ K and critical temperature of $282.75 \leq T_c \leq 699.15$ K. Total average percent error for M-Z equation based on Table 2 results is 2.3702, and for the C-C equation is 3.2952, which indicates that the M-Z equation is 68 percent more accurate than the C-C equation. Comparison of M-Z VPE with experimental data with average percent of error of 2.3702 depicts accuracy and applicability of the new proposed equation for practical and engineering applications.

CONCLUSION AND REMARKS

The new generalized equation, the M-Z equation, which is as simple as the C-C equation, calculates vapor pressure of pure substances with acceptable precision. In order to utilize this equation, critical temperature, critical pressure and normal boiling point are the necessary parameters. According to the simplicity, generality and precision of the new equation, it can be used when we have no special equation to calculate the vapor pressure of pure substances. The proposed equation is superior to the C-C equation and fits experimental data better than the C-C equation.

NOMENCLATURE

T_b : normal boiling point [K]
T_C : critical temperature [K]
P_C : critical pressure [MPa]
A, B : coefficient of new equation (Eq. (7)) and previous model

(Eq. (3))
P_r : reduced pressure [Mpa]
ΔH_{vap} : heat of vaporization
N   : number of data points used in the fitting
P   : pressure
R   : gas constant
T   : temperature [K]
Z   : compressibility

Greek Letters
τ : inverse of the reduced temperature [$1/T_r$]

Subscripts
b   : boiling point
c   : critical
cal   : calculated
exp   : experimental
equ   : equation
r   : reduced
v   : vapor

REFERENCES

1. W. C. Edmister and B. I. Lee, *Applied hydrocarbon thermodynamics*, Vol. 1, Gulf Publishing Co., Houston (1986).
2. C. H. Whitson, *SPE journal*, 685-696 (1984).
3. K. R. Hall and L. Yarbourough, *OGJ*, 82-92 (1973).
4. R. P. Sutton and F. F. Farshad, *Evaluation of empirically derived PVT properties for Gulf of Mexico crude oils*, SPE Paper 13172, Proceedings of the 59th Annual SPE Technical Conference, Houston (1984).
5. J. M. Campbell, *Gas conditioning and processing*, Campbell Petroleum Series, Vol. 1, Norman, Okla. (1960).
6. T. E. Daubert, *Chemical engineering thermodynamics*, Chapter Six, Mc.Graw-Hill (1985).
7. T. E. Daubert and D. K. Jones, *Pure component liquid vapor pressure measurements*, Project 821, AIChE Symp., Ser. 86, (1990).
8. M. Reinhard and A. Drefahl, *Handbook for estimating physicochemical properties of organic compounds*, Wiley & Sons, New York (1999).
9. H. Nishiumi, H. Akita and S. Akiyama, *Korean J. Chem. Eng.*, **14**, 359 (1997).
10. C. Kwak and T. F. Anderson, *Korean J. Chem. Eng.*, **8**, 88 (1991).
11. E. S. Goll and P. C. Jurs, *J. Chem. Inf. Comput. Sci.*, **39**, 1081 (1999).
12. H. W. Xiang, *Int. J. Thermophys*, 22 (2001).
13. W. Wagner, *Cryogenics*, **13**, 470 (1973).
14. Kh. Mejbri and A. Bellagi, *Thermochimica Acta*, **436**, 140 (2005).
15. R. C. Reid, J. M. Prausnitz and B. E. Poling, *The properties of gases and liquids*, fourth ed., McGraw-Hill, 205-240 (1987).
16. B. E. Poling, J. M. Prausnitz and J. P. O'Connell, *The properties of gases and liquids*, fifth ed., McGraw-Hill (2001).
17. P. J. Linstrom and W. G. Mallard (Eds.), *NIST chemistry webBook*, NIST Standard Reference Database Number 69 (http://webbook.nist.gov) (2001).
18. H. P. Robert, *Perry's chemical engineers' handbook*, sixth edition, section 3 (1984).