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# A REFERENCE VALUE METHOD OF THE CORRESPONDING STATES PRINCIPLE FOR THE PREDICTION OF LATENT HEATS OF VAPORIZATION OF PURE LIQUIDS *

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## ABSTRACT

Based on a reference value method of the corresponding states principle, a generalized equation for the latent heat of vaporization of liquid is developed. The latent heats of vaporization calculated with the proposed equation are compared with the corresponding experimental values presented in the literature for 71 compounds, involving a total of 2695 data points. These comparisons are further examined using the results of the Watson equation (1943), the Fish and Lielmezs equation (1975) and the Xu Zhong equation (1984). The results of these comparisons indicate that the proposed equation is more accurate than the other three equations.

## INTRODUCTION

The latent heat of vaporization is an indispensable physical property for the design and development of industrial processes at elevated temperatures. It is usually not convenient to determine all the required data experimentally. Hence a correlation is needed to estimate values or to extend or extrapolate limited available data from the freezing point all the way to the critical temperature. Watson [1], Fish and Lielmezs [2], Xu Zhong [3], and others, have proposed equations that may be used to estimate the latent heats of vaporization of pure compounds at different temperatures once the value at the normal boiling point is known. The prediction of the latent heat of vaporization is discussed in many publications. Reid et al. [4] present excellent summaries of the previous work in this area.

We have recently developed a reference value method of the corresponding states principle (RVMCSP) [5] based on a multiparameter corresponding

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states principle [6]. We apply the RVMCSP to develop a generalized equation for predicting the latent heat of vaporization of pure compounds in this study. The pure compound parameters required are the same as those used by the equations of Watson, Fish and Lielmezs, and Xu Zhong.

## DEVELOPMENT OF THE GENERALIZED EQUATION

In this section we first consider the reference value method of the corresponding states principle (RVMCSP), and then apply the RVMCSP to derive the generalized equation for the latent heat of vaporization of a liquid.

Based on the multiparameter corresponding states principle [6], any fluid property $G$ has the following reduced equation of state

$$G_r = \frac{G(T,\ P)}{G_c(T_c,\ P_c)} = G_R(T_r,\ P_r,\ W_c,\ W_p,\ W_a,\ W_q) \tag{1}$$

where $G_c$ is the critical temperature $T_c$ and critical pressure $P_c$ dependence of the characteristic parameter pertaining to property $G$; $T_r = T/T_c$ is the reduced temperature; $P_r = P/P_c$ is the reduced pressure; and $W_c$, $W_p$, $W_a$ and $W_q$ are, respectively, the configurational, polar, associated and quantum factors. We now assume that there are properties $A$ and $B$ whose reduced equations have the forms

$$A_r = \frac{A(T,\ P)}{A_c(T_c,\ P_c)} = A_R^{[1]}(T_r)A_R^{[2]}(P_r)A_R^{[3]}(W_c,\ W_p,\ W_a,\ W_q) \tag{2}$$

$$Br = \frac{B(T,\ P)}{B_c(T_c,\ P_c)} = B_R^{[1]}(T_r,\ W_c)B_R^{[2]}(P_r,\ W_c)B_R^{[3]}(W_c,\ W_p,\ W_a,\ W_q) \tag{3}$$

where $A_r$ and $B_r$ are the reduced properties. If the values of the properties $A$ and $B$ at a reference temperature $T_0$ and a pressure $P$ are known, taking $A(T_0,\ P)$ and $B(T_0,\ P)$ as the reference values gives the equations

$$\frac{A(T,\ P)}{A(T_0,\ P)} = \frac{A_R^{[1]}(T_r)}{A_R^{[1]}(T_{0r})} \tag{4}$$

$$\frac{B(T,\ P)}{B(T_0,\ P)} = \frac{B_R^{[1]}(T_r,\ W_c)}{B_R^{[1]}(T_{0r},W_c)} \tag{5}$$

where $T_{0r} = T_0/T_c$. Using these two equations we can predict properties $A$ and $B$ at different temperatures from those at a reference temperature. If the values of the properties $A$ and $B$ at a temperature $T$ and a reference pressure $P_0$ are known, taking $A(T, P_0)$ and $B(T, P_0)$ as the reference values gives the equations

$$\frac{A(T, P)}{A(T, P_0)} = \frac{A_R^{[2]}(P_r)}{A(P_{0r})} \tag{6}$$

$$\frac{B(T, P)}{B(T, P_0)} = \frac{B_R^{[2]}(P_r, W_c)}{B_R^{[2]}(P_{0r}, W_c)} \tag{7}$$

where $P_{0r} = P_0/P_c$. Using these two equations, we can predict properties $A$ and $B$ at different pressures from those at a reference pressure. Equations (4)–(7) are the RVMCSP basic equations. These equations provide a basis for developing new equations for predicting fluid properties for large classes of compounds and mixtures. We have successfully applied eqn. (4) to develop the equations for predicting surface and interfacial tensions of pure liquids and liquid mixtures [5].

We now begin to develop the generalized equation to the latent heat of vaporization. Based on the RVMCSP, from eqn. (4), the generalized equation for the latent heat of vaporization can be expressed as

$$\frac{H_v(T)}{H_v(T_0)} = \frac{H_R(T_r)}{H_R(T_{0r})} \tag{8}$$

where $H_v(T)$ is the latent heat of vaporization at the temperature of interest, $T$; $H_v(T_0)$ is the latent heat of vaporization at a reference temperature $T_0$; and $H_R$ is a universal function of the reduced temperature. The function $H_R$ can be expressed as

$$H_R(T_r) = (1 - T_r)^n (a + bT_r + cT_r^2) \tag{9}$$

where $n$, $a$, $b$, and $c$ are universal constants which are independent of the compounds. The term of $(1 - T_r)$ is introduced by considering that the latent heat of vaporization is equal to zero at the critical point for any compound. Using the normal boiling temperature, $T_b$, as the reference temperature and substituting eqn. (9) into eqn. (8) yields

$$\frac{H_v(T)}{H_v(T_b)} = \left(\frac{1 - T_r}{1 - T_{br}}\right)^n \left(\frac{a + bT_r + cT_r}{a + bT_{br} + cT_{br}}\right) \tag{10}$$

where $T_{br} = T_b/T_c$. We obtained $n = 0.38$, $a = 10$, $b = 3$, and $c = 2$ from the latent heat data of water [7]. Thus, we have

$$\frac{H_v(T)}{H_v(T_b)} = \left(\frac{1 - T_r}{1 - T_{br}}\right)^{0.38} \left(\frac{10 + 3T_r + 2T_r}{10 + 3T_{br} + 2T_{br}}\right) \tag{11}$$

Equation (11) is our proposed generalized equation for the prediction of latent heats of vaporization of pure liquids at different temperatures.

TABLE 1

Deviations between experimental and predicted latent heats

| Compounds | Temp. range $T_r$ | No. of points | Average absolute deviation (%) | | | |
|---|---|---|---|---|---|---|
| | | | This work | Watson eqn. | FL eqn. | Xu eqn. |
| *Inorganic* | | | | | | |
| *Monatomic, diatomic* | | | | | | |
| Helium | 0.4239–0.9981 | 18 | 13.64 | 13.84 | 25.15 | 17.06 |
| Argon | 0.5553–0.9943 | 69 | 3.20 | 3.42 | 2.42 | 0.56 |
| Krypton | 0.5528–0.9933 | 47 | 2.76 | 2.98 | 2.05 | 1.35 |
| Xenon | 0.5570–0.9941 | 65 | 2.40 | 2.77 | 1.38 | 1.30 |
| Chlorine | 0.4391–0.9984 | 24 | 1.28 | 1.49 | 2.22 | 1.64 |
| Fluorine | 0.6584–0.9875 | 20 | 1.64 | 1.85 | 2.39 | 1.66 |
| Oxygen | 0.3512–0.9950 | 102 | 3.00 | 3.52 | 1.90 | 1.21 |
| *Polyatomic* | | | | | | |
| Water | 0.4220–0.9998 | 96 | 0.89 | 1.38 | 2.26 | 1.18 |
| Sulphur dioxide | 0.7504–0.9826 | 18 | 3.55 | 3.74 | 4.27 | 3.53 |
| Carbon dioxide | 0.7119–0.9961 | 43 | 1.05 | 1.38 | 1.95 | 1.56 |
| *Organic* | | | | | | |
| *Alkanes* | | | | | | |
| Methane | 0.4776–0.9971 | 29 | 2.62 | 2.88 | 3.48 | 3.13 |
| Propane | 0.5122–0.9924 | 18 | 1.08 | 1.30 | 1.81 | 1.28 |
| Isobutane | 0.3017–0.9878 | 29 | 1.36 | 2.08 | 1.68 | 1.67 |
| *n*-Pentane | 0.3260–0.6666 | 17 | 0.23 | 1.33 | 0.55 | 0.32 |
| Isopentane | 0.2672–0.6795 | 20 | 0.30 | 1.54 | 0.94 | 0.57 |
| *n*-Hexane | 0.3606–0.9907 | 33 | 1.46 | 2.11 | 1.50 | 1.89 |
| *n*-Heptane | 0.3391–0.9870 | 36 | 0.55 | 1.04 | 2.00 | 1.10 |
| *n*-Octane | 0.3919–0.9891 | 35 | 0.98 | 0.88 | 2.19 | 1.18 |
| 2,2,4-Trimethylpentane | 0.3181–0.9980 | 38 | 1.00 | 1.85 | 3.06 | 1.35 |
| *n*-Nonane | 0.3749–0.9966 | 38 | 1.08 | 1.70 | 4.30 | 1.17 |
| *n*-Decane | 0.4089–0.9903 | 37 | 1.03 | 0.68 | 3.54 | 0.94 |
| *Naphthenes* | | | | | | |
| Cyclopentane | 0.3579–0.9832 | 33 | 0.60 | 1.11 | 1.06 | 0.66 |
| Methylcyclopentane | 0.2499–0.9820 | 40 | 0.70 | 1.77 | 1.35 | 1.26 |
| Ethylcyclopentane | 0.2514–0.9889 | 43 | 1.60 | 2.68 | 2.71 | 1.87 |
| 1,1-Dimethylcyclopentane | 0.3874–0.9691 | 33 | 2.21 | 2.70 | 1.82 | 2.68 |
| Cyclohexane | 0.5120–0.9821 | 27 | 1.12 | 1.27 | 0.62 | 1.97 |
| Methylcyclohexane | 0.2676–0.9841 | 42 | 0.74 | 1.73 | 1.75 | 1.06 |
| Ethylcyclohexane | 0.2678–0.9737 | 44 | 3.15 | 3.63 | 2.53 | 3.30 |

TABLE 1 (continued)

| Compounds | Temp. range $T_r$ | No. of points | Average absolute deviation (%) | | | |
|---|---|---|---|---|---|---|
| | | | This work | Watson eqn. | FL eqn. | Xu eqn. |
| *Olefins* | | | | | | |
| Propylene | 0.2552–0.9948 | 28 | 1.62 | 2.03 | 2.40 | 1.56 |
| 1-Butene | 0.2220–0.9847 | 33 | 1.00 | 1.27 | 1.31 | 1.25 |
| *cis*-2-Butene | 0.3343–0.9883 | 29 | 1.51 | 2.06 | 2.60 | 1.91 |
| *Trans*-2-Butene | 0.4044–0.9883 | 26 | 0.90 | 1.35 | 1.02 | 1.45 |
| Isobutene | 0.3186–0.9886 | 29 | 0.94 | 1.70 | 1.04 | 1.44 |
| 1-Pentene | 0.2386–0.9979 | 37 | 0.87 | 1.51 | 1.81 | 0.85 |
| *cis*-2-Pentene | 0.2586–0.9727 | 35 | 1.51 | 2.31 | 1.36 | 1.94 |
| *Trans*-2-Pentene | 0.2802–0.9747 | 34 | 1.22 | 2.03 | 1.19 | 1.78 |
| 1-Hexene | 0.2839–0.9782 | 36 | 0.83 | 1.65 | 1.58 | 1.29 |
| 1-Heptene | 0.3594–0.9926 | 35 | 0.60 | 1.19 | 2.96 | 1.12 |
| 1-Octene | 0.3056–0.9938 | 40 | 1.37 | 2.05 | 4.35 | 2.23 |
| Cyclopentene | 0.2828–0.9743 | 36 | 1.55 | 2.26 | 1.49 | 1.93 |
| Cyclohexene | 0.3090–0.9692 | 38 | 2.58 | 3.21 | 2.20 | 2.90 |
| Propadiene | 0.3635–0.9982 | 26 | 2.75 | 3.19 | 3.05 | 2.32 |
| 1,3-Butadiene | 0.4073–0.9770 | 47 | 0.91 | 0.80 | 2.14 | 1.38 |
| Isoprene | 0.2750–0.9566 | 34 | 4.31 | 3.80 | 3.80 | 4.56 |
| *Aromatics* | | | | | | |
| Benzene | 0.7980–0.9993 | 47 | 5.38 | 5.41 | 5.92 | 6.66 |
| Tolulene | 0.3084–0.9818 | 41 | 0.48 | 1.23 | 1.19 | 0.90 |
| *o*-Xylene | 0.4008–0.9866 | 38 | 0.92 | 1.05 | 2.12 | 0.93 |
| *m*-Xylene | 0.3766–0.9903 | 39 | 0.73 | 1.28 | 2.19 | 1.07 |
| *n*-Xylene | 0.4742–0.9919 | 33 | 0.94 | 1.22 | 2.30 | 0.60 |
| Ethylbenzene | 0.2956–0.9735 | 43 | 0.97 | 1.10 | 1.76 | 0.71 |
| Isopropylbenzene | 0.2879–0.9769 | 45 | 0.73 | 1.45 | 2.00 | 1.23 |
| *n*-Butylbenzene | 0.2922–0.9730 | 46 | 1.37 | 0.67 | 1.81 | 0.61 |
| Biphenyl | 0.4658–0.8402 | 16 | 3.38 | 3.06 | 2.50 | 3.65 |
| Naphthalene | 0.4833–0.9891 | 39 | 1.16 | 1.32 | 2.71 | 1.87 |
| *Acetylenes* | | | | | | |
| Methylacetylene | 0.4321–0.9810 | 23 | 0.53 | 0.84 | 0.72 | 0.75 |
| 1-Butyne | 0.3303–0.9774 | 31 | 0.70 | 0.70 | 1.12 | 0.54 |
| 2-Butyne | 0.4981–0.9898 | 25 | 0.51 | 0.81 | 0.86 | 1.24 |
| *Halogenated hydrocarbons* | | | | | | |
| Methyl chloride | 0.5121–0.8004 | 25 | 0.20 | 0.20 | 0.33 | 0.66 |
| Trichloromonofluoromethane | 0.4524–0.8769 | 62 | 0.27 | 0.33 | 0.48 | 0.28 |
| Dichlorodifluoromethane | 0.5277–0.9953 | 79 | 1.13 | 1.35 | 1.73 | 0.84 |
| Monochlorotrifluoromethane | 0.5397–0.9896 | 69 | 0.91 | 1.11 | 1.76 | 1.30 |
| Dichloromonofluoromethane | 0.4723–0.9996 | 120 | 1.35 | 1.38 | 0.56 | 2.15 |

TABLE 1 (continued)

| Compounds | Temp. range $T_r$ | No. of points | Average absolute deviation (%) | | | |
|---|---|---|---|---|---|---|
| | | | This work | Watson eqn. | FL eqn. | Xu eqn. |
| *Halogenated hydrocarbons* | | | | | | |
| Monochlorodifluoromethane | 0.4691–0.9946 | 73 | 0.58 | 0.63 | 1.18 | 1.56 |
| Trichlorotrifluoroethane | 0.4990–0.7248 | 23 | 0.25 | 0.25 | 0.46 | 0.22 |
| Dichlorotetrafluoroethane | 0.5565–0.7952 | 21 | 0.98 | 1.12 | 1.64 | 1.36 |
| Monochlorodifluoroethane | 0.5931–0.8614 | 23 | 2.11 | 1.99 | 1.16 | 3.29 |
| *Oxygen-containing compounds* | | | | | | |
| Methanol | 0.5323–0.9805 | 24 | 1.15 | 1.36 | 2.05 | 1.95 |
| 1-Propanol | 0.5088–0.9931 | 27 | 7.17 | 7.20 | 4.13 | 7.19 |
| Ethyl ether | 0.6492–0.9919 | 17 | 0.70 | 0.83 | 2.18 | 1.05 |
| Phenyl ether | 0.6622–0.7988 | 12 | 1.33 | 1.23 | 0.54 | 2.22 |
| Ethyl acetate | 0.6749–0.9807 | 17 | 2.17 | 2.35 | 1.10 | 1.42 |

## RESULTS AND DISCUSSIONS

The generalized equation described above was tested by predicting the latent heats of vaporization for 71 compounds involving a total of 2695 data points and the results compared with the corresponding experimental values presented in the literature [7]. The average absolute deviations are summarized in Table 1. The results of the proposed equation have been compared with those produced by the other three equations, namely, the Watson equation [1], the Fish–Lielmezs (FL) equation [2], and the Xu equation [3]. The deviations produced by these three equations are also presented in Table 1.

It can be seen from Table 1 that, for most compounds, the deviations calculated with the proposed equation are smaller than those calculated with the other three equations. The average deviations exceeding 3% are: 8 for the proposed equation, 11 for the Watson equation, 11 for the FL equation, and 9 for the Xu equation. For deviations less than 1%, the proposed equation, the Watson equation, the FL equation, and the Xu equation account for 29, 12, 10 and 17, respectively.

In order to form an opinion on the capability of each of these equations to estimate the latent heat of vaporization for compounds corresponding to their respective classification, the results in Table 1 have been summarized in Table 2. A review of the deviations presented in Table 2 indicates that the generalized equation developed in this study has the greatest accuracy with

TABLE 2

Summary of deviations according to classes of compounds

| Class of compound | No. of compounds | No. of points | Average absolute deviation (%) | | | |
|---|---|---|---|---|---|---|
| | | | This work | Watson eqn. | FL eqn. | Xu eqn. |
| *Inorganic* | | | | | | |
| Monatomic, diatomic | 7 | 345 | 3.25 | 3.59 | 3.19 | 2.00 |
| Polyatomic | 3 | 157 | 1.24 | 1.65 | 2.40 | 1.55 |
| *Organic* | | | | | | |
| Alkanes | 11 | 330 | 1.10 | 1.57 | 2.48 | 1.37 |
| Naphthenes | 7 | 262 | 1.49 | 2.21 | 1.78 | 1.85 |
| Olefins | 16 | 543 | 1.51 | 2.00 | 2.17 | 1.87 |
| Aromatics | 10 | 387 | 1.56 | 1.75 | 2.49 | 1.79 |
| Acetylenes | 3 | 79 | 0.59 | 0.78 | 0.92 | 0.82 |
| Halogenated hydrocarbons | 9 | 495 | 0.91 | 1.00 | 1.05 | 1.36 |
| Oxygen-containing compounds | 5 | 97 | 2.95 | 3.05 | 2.30 | 3.19 |
| Over all | 71 | 2695 | 1.59 | 1.93 | 2.12 | 1.72 |

the exception of monatomic and diatomic compounds for which the generalized equation is less accurate than the FL and Xu equations, and oxygen-containing compounds for which the generalized equation is less accurate than the Xu equation.

The results in Table 2 show that the generalized equation gives the lowest overall average deviation of 1.59% for the 71 compounds involving 2695 data points, but using the capability of the Watson equation, the FL equation, and Xu equation, these deviations are found to be 1.93%, 2.12%, and 1.72%, respectively. Obviously, the generalized equation developed in this work is a more accurate method than the others for the prediction of the latent heat of vaporization.

## CONCLUSIONS

We have applied the reference value method of the corresponding states principle to develop the generalized equation for predicting the latent heat of vaporization of pure compounds. Good agreement between the predicted and experimental latent heats of vaporization is obtained. Further work is in progress to apply the RVMCSP to develop equations for the prediction of other thermodynamic and transport properties of fluids.

## LIST OF SYMBOLS

| | |
|---|---|
| $a$, $b$, $c$ | universal constants |
| $A$, $B$, $G$ | properties of fluids |
| $H_v$ | heat of vaporization |
| $n$ | universal constant |
| $P$ | pressure |
| $T$ | absolute temperature |

### *Subscripts*

| | |
|---|---|
| b | property at normal boiling point |
| c | critical state or characteristic parameter |
| r | reduced state |
| R | universal function |

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