Thermochimica Acta, 90 (1985) 125–133
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CORRELATION OF VAPOR PRESSURES OF PURE SUBSTANCES IN HOMOLOGOUS SERIES

MAREK ROGALSKI

Institute of Physical Chemistry of the Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw (Poland)

(Received 13 February 1985)

ABSTRACT

An equation for correlating the vapor pressures of pure substances is developed. When this equation is used with reliable thermal data (ΔH^{v} and ΔC_{p}^0 at 298.15 K) it can be applied for:

(1) checking the consistency of vapor pressure data;

(2) extrapolation to the low pressure region.

It was observed that for homologous series, parameters of the proposed equation vary smoothly. It enables the formulation of a general correlation of vapor pressures of substances belonging to a given homologous series.

INTRODUCTION

Vapor pressure data in the subatmospheric range of pressures are usually represented by empirical three- or four-parameter equations, e.g., Antoine, Cragoe, and many others. The parameters of these equations have no physical meaning. For this reason they are not suitable for extrapolation. Neither can it be expected that parameters will vary smoothly in a homologous series. Hence, a possible generalization of these equations for representing vapor pressures of compounds belonging to a given homologous series is doubtful.

For this purpose, equations resulting from integration of the Clapeyron equation are preferable. Exact integration of the Clapeyron equation is only possible when information about volumetric and thermal properties of the substances in question is available. The short supply of experimental data of this kind makes this method of little practical use. Wexler and Greenspan [1] performed such an integration for water in the temperature range 298.15–373.15 K. Both the enthalpy of vaporization, ΔH^{v}, and the volumetric term of the Clapeyron equation were expressed by polynomials of

0040-6031/85/$03.30

temperature. Integration yielded the following equation

$$\ln(p)=\sum_{i=0}^{5}A_iT^{i-1}+A_6\ln T \tag{1}$$

where the coefficients A_i are combinations of the corresponding terms in polynomials expressing thermal and volumetric properties.

Equation (1) can represent high-precision vapor pressure experimental data of water. The authors observed that this can also be obtained when eqn. (1) is reduced to a five-parameter form and is fitted directly to vapor pressure data. It is the result of a partial compensation of thermal and volumetric terms. This effect of compensation explains how vapor pressure data in the subatmospheric pressure range can be accurately represented by simple but flexible three-parameter equations, e.g., the Antoine equation. As mentioned above, these equations cannot be used with success for extrapolation down to the low pressure region. They are also unable to detect the "sour" experimental points as was pointed out by Scott and Osborn [2]. On the other hand, the effect of compensation means that the fit of eqn. (1) to experimental vapor pressure data cannot give physically meaningful parameters.

In this situation the best solution is to fit a simplified form of eqn. (1) to vapor pressure and thermal properties simultaneously. This approach was successfully applied by King and Al-Najjar [3], Ambrose and Davies [4] and Scott and Osborn [2]. The lack of thermal data is the main obstacle for the wide application of this approach. The purpose of this article is to investigate the possibility of designing an equation to represent vapor pressures retaining the advantages of forms resulting from the exact integration of the Clapeyron equation (physically meaningful parameters) and using the minimum necessary thermal data.

DEVELOPMENT OF THE METHOD

We follow the procedure proposed by King and Al-Najjar [3] which was further developed by Ambrose and Davies [4]. These authors showed that for pressures low enough to express volumetric properties of a gas by the virial equation of state limited to the second term we can write

$$F=\frac{\mathrm{d}}{\mathrm{d}T}\left[RT^2\left(\frac{\mathrm{d}\ln p}{\mathrm{d}T}\right)_{\mathrm{s}}\right]=C_{\mathrm{p}}^0-C_{\mathrm{p}}^{\mathrm{l}}-G=\Delta C_{\mathrm{p}}^0-G \tag{2}$$

$$G=T\left[p\frac{\mathrm{d}^2B}{\mathrm{d}T^2}+2\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_{\mathrm{s}}\left(\frac{\mathrm{d}B}{\mathrm{d}T}-\frac{\mathrm{d}V^{\mathrm{l}}}{\mathrm{d}T}\right)+\left(\frac{\mathrm{d}^2p}{\mathrm{d}T^2}\right)_{\mathrm{s}}(B-V^{\mathrm{l}})\right] \tag{3}$$

where C_{p}^0 is the ideal gas heat capacity, $C_{\mathrm{p}}^{\mathrm{l}}$ is the liquid heat capacity, B is the second virial coefficient and V^{l} is the molar volume of the liquid.

Expressing F as a quadratic function of T and combining with eqn. (2) we obtain, after two integrations, an equation formally identical to eqn. (1)

$$\ln(p/p_0) = \sum_{i=0}^{3} A_i T^{i-1} + A_4 \ln(T/T_0) \tag{4}$$

where p_0 and T_0 are the arbitrarily chosen saturation pressure and the corresponding temperature, respectively. Ambrose and Davies [4] simultanously fitted eqn. (4) to vapor pressure and ΔC_p^0 data, obtaining a set of parameters A_i enabling the successful extrapolation of vapor pressures to the low pressure region. This method is applicable only in the case when ΔC_p^0 can be represented as a function of temperature. We modify this procedure by limiting the necessary thermal data to the set of ΔH^v and ΔC_p^0 at one reference temperature. This temperature was chosen to be $T_\mathrm{ref} = 298.15$ K for two reasons: (1) thermal data at this temperature are most accessible and most reliable; (2) the term G (eqn. 3) at this temperature is usually small. We observed that

$$E = RT\left(\frac{\mathrm{d}\ln p}{\mathrm{d}T}\right)_\mathrm{S} = \Delta H^\mathrm{v} - G1 \tag{5}$$

$$G1 = T\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_\mathrm{S}(B - V^\mathrm{l}) \tag{6}$$

Introducing eqn. (7) into eqn. (2)

$$F = (F)_{T=T_\mathrm{ref}} + b(T - T_\mathrm{ref}) + c(T^2 - T_\mathrm{ref}^2) \tag{7}$$

we perform two integrations: the first one from $T = T_\mathrm{ref}$ to T and the second one from $T = T_0$ to T. For most cases we chose T_0 as the boiling point of the substance in question. We get an equation formally identical to eqn. (4) but with the following meanings of the parameters A_i

$$A_0 = (-E + FT - bT^2/2 - 2cT^3/3)_{T=T_\mathrm{ref}}/R \tag{8a}$$

$$\begin{aligned} A_1 = \big[&-(-E + FT)/T_0 + \ln(T_0)(-F + T(b - cT)) \\ &+ T^2(b/2 + 2cT/3)/T_0 - T_0(b/2 - cT_0/6)\big]_{T=T_\mathrm{ref}}/R \end{aligned} \tag{8b}$$

$$A_2 = b/2/R \tag{8c}$$

$$A_3 = c/6/R \tag{8d}$$

$$A_4 = [F - T(b + cT)]_{T=T_\mathrm{ref}}/R \tag{8e}$$

Inspection of the newly defined meaning of the parameters of eqn. (4) shows that the values of the first and second derivatives of the pressure on temperature at $T = T_\mathrm{ref}$ are fixed by thermal data.

Fitting eqn. (4) to vapor pressure data we find the values of the parameters b and c which express simultaneous change of thermal and volumetric data with temperature. Attempting to apply the proposed equation in representing the vapor pressures of substances belonging to a homologous series we observe the following.

(1) The values of ΔH^{v} and $\Delta C_{\mathrm{p}}^{0}$ can be fitted to a polynomial equation which is the function of number of carbon atoms or boiling points of members of a given series. This procedure allows the "most consistent" set of thermal data to be found, and, at the same time, makes the calculation of missing data possible.

(2) The two parameters b and c found from fitting the experimental vapor pressure data are expected to change regularly in homologous series. If this is the case, then eqn. (4) can be presented in a general form valid for each member of a given homologous series.

APPLICATION OF THE METHOD

The method described above was applied to the correlation of vapor pressures of two homologous series: *n*-alkanes and *n*-alkanols. Vapor pressure data of *n*-alkanes used for calculation were those of Forziatti et al. [5] and Willingham et al. [6]. These authors measured vapor pressures for all members of the series from *n*-pentane to *n*-hexadecane over the range of pressures 7–100 kPa. For *n*-alkanols, the data of Ambrose and Sprake [7] were used [8]. They measured vapor pressures of *n*-alkanols from methanol to *n*-pentanol and for *n*-octanol, *n*-decanol, *n*-dodecanol, *n*-hexadecanol and *n*-octadecanol. For lower members of the series the measurements were performed up to 200 kPa. Enthalpy of vaporization data were taken from the paper of Manson et al. [8]. These data were fitted to the polynomial function in N (number of carbon atoms) and the results are presented in Table 1. Liquid heat capacities of *n*-alkanes were taken from the work of Messerly et

TABLE 1

Auxiliary data for the correlation of vapor pressure of *n*-alkanes and *n*-alkanols

n-Alkanes
$\Delta C_{\mathrm{p}}^{0} = -18.8 - 4.76N - 0.137N^2$ (J mol^{-1} K^{-1})
$\Delta H^{\mathrm{v}} = 1.892 + 4.953N$ (kJ mol^{-1})
$G = -60.6 + 11.80N - 0.5893N^2$ (J mol^{-1} K^{-1})
$G1 = -4486 + 9573.9N - 51.50N^2$ (J mol^{-1})
for $N > 10$; $G = G1 = 0$

n-Alkanols
$\Delta C_{\mathrm{p}}^{0} = -28.0 - 9.48N$ (J mol^{-1} K^{-1})
$\Delta H^{\mathrm{v}} = 33.160 + 4.6771N$ (kJ mol^{-1})
$G = -774.2 + 233.77N - 17.238N^2$ (J mol^{-1} K^{-1})
$G1 = -7.4 + 0.985N$
for $N > 8$; $G = G1 = 0$

TABLE 2

Representation of vapor pressure data of *n*-alkanes [5,6] with eqn. (4)

N (C_NH_{2N+2})	Standard deviation of pressure, $s(p)$ (kPa), resulting from		
	optimization of five parameters	optimization of parameters b and c	general correlation
5	0.006	0.007	0.008
6	0.008	0.012	0.012
7	0.009	0.008	0.012
8	0.007	0.006	0.006
9	0.003	0.005	0.006
10	0.002	0.007	0.007
11	0.005	0.006	0.007
12	0.006	0.007	0.012
13	0.008	0.009	0.009
14	0.018	0.017	0.016
15	0.009	0.011	0.010
16	0.010	0.014	0.020

al. [9], and of *n*-alkanols from papers of Fortier and Benson [10], Rećko [11], Kalinowska [12], Kalinowska and Wóycicka [13]. The ideal heat capacity of the gas was taken from API 44 tables [14] for *n*-alkanes and from TRC tables [15] for *n*-alkanols. Values of ΔC_p^0 calculated from these data were fitted to a polynomial equation of N and the resulting coefficients are also presented in Table 1. Second virial coefficients and their temperature derivatives were calculated using the method of Tsonopoulos [16]. Calculated values of $G1$ and G were fitted to the polynomial equation of T_b (boiling point) and the results are also given in Table 1. Using auxiliary data from Table 1, together with boiling points, the vapor pressure data of all substances considered were fitted to eqn. (4). The parameters b and c were found for each compound. Standard deviations, $s(p)$, of pressure are given in Table 2 together with those resulting from the fit of vapor pressures to eqn. (4), when all five parameters are optimized (ΔH^v, ΔC_p^0 and p_0 are considered as adjustable parameters).

The parameters b and c change smoothly with the *n*-alkane or *n*-alkanol chain length and can be presented as polynomial functions in N or in T_b (boiling point). The resulting equations for b and c for both homologous series are, for *n*-alkanes

$$b = -0.9114 + 0.34341 \times 10^{-3} T_b + 0.24239 \times 10^{-5} T_b^2 \tag{9a}$$

$$c = 0.25857 \times 10^{-2} - 0.41244 \times 10^{-5} T_b \tag{9b}$$

for *n*-alkanols

$$b = -2.3826 - 0.4587N + 0.05056N^2 - 0.27691 \times 10^{-2} N^3$$

$$+0.5506 \times 10^{-4} N^4 \quad (10a)$$

$$c = 0.00460 + 0.0008N \quad (10b)$$

In both cases the parameter c changes linearly with the chain length. The parameter b for *n*-alkanes is a quadratic function of the boiling points. For *n*-alkanols, the function describing the behavior of b is more complicated. Equation (4), used with auxiliary data from Table 1 and the values of the parameters b and c calculated from eqns. (9) or (10), can be considered as a predictive method. In fact, this set of equations enables the calculation of the vapor pressure of any compound belonging to a given homologous series. The last column of Table 2 shows standard deviations, $s(p)$, resulting from a comparison of experimental and predicted data.

For *n*-alkanes, the result of the correlation is very satisfactory. For most of the members of the homologous series the mean deviation in pressure resulting from the general correlation is close to the dispersion of the experimental data. (Comparison of $s(p)$ in the first and third columns of Table 2.) For *n*-alkanols the results are not so good. For *n*-decanol a comparison of experimental and calculated data yields $s(p)$ as high as 0.1 kPa. For other alkanols, the results are better. There are a number of reasons for this. First, thermal data for *n*-alkanols are scarce and their accuracy is not exactly known. The experimental data of Ambrose cover, for lower alkanols, the pressure range up to 200 kPa. At the upper limit of pressure, the possible absolute error in pressure increases. When eqn. (4) yields $s(p)$ values (second column of Table 3) substantially greater than the dispersion of experimental data (first column of the same table) it proves that some inconsistency exists between thermal data and vapor pressure data. This inconsistency further distorts the results of the general correlation (the

TABLE 3

Representation of vapor pressure data of *n*-alkanols [7] with eqn. (4)

N ($C_NH_{2N+1}OH$)	Standard deviation of pressure, $s(p)$ (kPa), resulting from		
	optimization of five parameters	optimization of parameters b and c	general correlation
1	0.009	0.009	0.026
2	0.011	0.020	0.028
3	0.005	0.010	0.018
4	0.003	0.007	0.021
5	0.003	0.037	0.066
8	0.010	0.011	0.039
10	0.012	0.037	0.079
12	0.018	0.033	0.095
16	0.008	0.014	0.045
18	0.010	0.016	0.018

increase in $s(p)$ in the third column compared to that of the second). This effect can be observed for *n*-alkanols in Table 3. Another possible reason is that a simple polynomial equation (eqn. 7) does not adequately represent the temperature dependence of the term F. Certainly, the temperature dependence of thermal properties of *n*-alkanols can be complicated by association phenomena. Viewing all these factors, the results of the correlation (third column of Table 3) can be considered as acceptable.

EXTRAPOLATION TO THE LOW PRESSURE REGION

As was shown in the previous section, eqns. (1), (9) and (10) can be considered as a general correlation of vapor pressure data of substances belonging to a given homologous series. Thermal data included in this correlation should improve the quality of low pressure prediction. In Table 4 the results of a comparison of a few sets of low and very low pressure data with the values predicted by the proposed correlation method are presented.

The results of extrapolation for *n*-alkanes are quite satisfactory. Far temperature extrapolation for *n*-pentane (160 K) gives very good results, as

TABLE 4

Results of prediction of low pressure data using the proposed method

T (K)	P (kPa)	ΔP (kPa)	T (K)	P (kPa)	ΔP (kPa)
n-Hexanol [17]			*n*-Pentane [20]		
298.230	0.115	0.015	143.61	0.000081	−0.000018
303.151	0.160	0.011	150.51	0.000269	−0.000081
308.146	0.227	0.006	157.28	0.000767	−0.000316
313.217	0.335	0.010	179.60	0.01920	−0.0041
318.213	0.480	0.012	189.41	0.0569	−0.0131
323.156	0.676	0.015	205.96	0.2853	−0.0587
328.211	0.949	0.021	218.97	0.9266	−0.0825
333.163	1.300	0.022	227.21	1.733	−0.082
338.176	1.773	0.027			
242.824	2.301	−0.005			
n-Octanol [18]			*n*-Hexadecane [19]		
328.03	0.142	0.001	299.05	0.000211	0.000000
337.26	0.281	0.003	304.15	0.000364	0.000001
343.59	0.431	0.000	309.25	0.000631	0.000018
347.06	0.544	0.001	323.05	0.00234	0.00007
350.84	0.700	0.006	333.15	0.00533	−0.00013
353.01	0.803	0.007	353.15	0.0260	0.0003
364.41	1.591	0.013	373.15	0.101	0.002
374.81	2.817	0.016	393.15	0.324	0.008
382.72	4.226	0.018	413.15	0.819	−0.059

for *n*-hexadecane. The best agreement is observed at very low pressures, which may be due to the characteristics of the experimental methods used by authors [19,20] (chromatographic and saturation methods). The results of Wieczorek [17] for *n*-hexanol and of Ambrose et al. [18] for *n*-octanol were compared with the predicted values. Any available vapor pressure data for *n*-hexanol were included in the data base of the proposed method. For both alkanols, the results of the prediction are reasonable.

CONCLUSION

It was shown that the introduction of the enthalpy of vaporization, ΔH^{v}, and of $\Delta C_{\mathrm{p}}^{0}$ at $T = 298.15$ K into the integrated form of the Clausius–Clapeyron equation yields an equation whose properties can be summarized as follows.

(1) With two adjustable parameters it can satisfactorily represent vapor pressure data (in the case where ΔH^{v} and $\Delta C_{\mathrm{p}}^{0}$ are reliable).

(2) In the case when the fit of the proposed equation gives a mean deviation of pressure greater than that resulting from the use of purely empirical equations, some systematic errors in the experimental vapor pressure data (or in the thermal data) must be present.

(3) Parameters b and c change smoothly in a given homologous series and the proposed equation can be presented as a general correlation for this series.

(4) The proposed equation or general correlation for homologous series can be used with success for low pressure extrapolation.

The thermal data needed for the proposed method (ΔH^{v} and $\Delta C_{\mathrm{p}}^{0}$ at $T = 298.15$ K) can be found in the literature for many compounds. When experimental data are lacking, the existing prediction method can be used. Hence, the proposed method of correlation can be extended to other homologous series or groups of substances or it can simply be applied to individual compounds.

REFERENCES

1 A. Wexler and L. Greenspan, J. Res. Natl. Bur. Stand., Sect. A, 75 (1971) 213.
2 D.W. Scott and A.G. Osborn, J. Phys. Chem., 83 (1979) 2714.
3 M.B. King and H.S.H. Al-Najjar, Chem. Eng. Sci., 29 (1974) 1003.
4 D. Ambrose and R.H. Davies, J. Chem. Thermodyn., 12 (1980) 871.
5 A.F. Forziatti, W.R. Norris and F.D. Rossini, J. Res. Natl. Bur. Stand., 43 (1949) 555.
6 C.J. Willingham, W.J. Taylor, J.M. Pignacco and F.D. Rossini, J. Res. Natl. Bur. Stand., 35 (1945) 219.
7 D. Ambrose and C.H.S. Sprake, J. Chem. Thermodyn., 2 (1970) 631.
8 M. Manson, P. Sellers, G. Stridh and S. Sunner, J. Chem. Thermodyn., 9 (1977) 91.

9 J.F. Messerly, G.B. Guthrie, S.S. Todd and H.L. Finke, J. Chem. Eng. Data, 12 (1967) 338.

10 J.L. Fortier and G.C. Benson, J. Chem. Thermodyn., 8 (1976) 411.

11 M. Rećko, Bull. Acad. Polon. Sci., Ser. Chim., 18 (1970) 5.

12 B. Kalinowska, Bull. Acad. Polon. Sci., Ser. Chim., 28 (1975) 9.

13 B. Kalinowska and M. Wóycicka, Bull. Acad. Polon. Sci., Ser. Chim., 21 (1973) 11.

14 Selected values of properties of hydrocarbons and related compounds, Americal Petroleum Institute Research Project 44, Texas A&M University, College Station, Texas, 1971.

15 Selected values of properties of chemical compounds, Thermodynamics Research Center of Data Project, Texas A&M University, College Station, Texas, 1972.

16 C. Tsonopoulos, Am. Inst. Chem. Eng. J., 20 (1974) 263.

17 S. Wieczorek, Thesis, Institute of Physical Chemistry, Polish Academy of Sciences, 1976.

18 D. Ambrose, J.H. Ellender and C.H.S. Sprake, J. Chem. Thermodyn., 6 (1974) 909.

19 F.T. Eggestsen, G.G. Seibert and F.H. Stross, Anal. Chem., 41 (1969) 1177.

20 G.F. Carruth and R. Kobyashi, J. Chem. Eng. Data, 18 (1973) 111.