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Extension of the UNIVAP group contribution method: enthalpies of vaporization of special alcohols in the temperature range from 313 to 358 K[1]

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Abstract

For the extension of the UNIVAP group contribution method (UNIversal heats of VAPorization) it was necessary to measure heats of vaporization of substances containing some special functional groups. Measurements were performed with a quasi-isothermal microcalorimeter in order to obtain enthalpies of vaporization of pure substances with the accuracy needed. Experiments were made in a temperature range from 313 to 358 K for 3-buten-1-ol, 1-penten-3-ol, 5-hexen-1-ol, 3,3-dimethyl-1-butanol, 2,4,4-trimethyl-1-pentanol and 2,2-dimethyl-3-pentanol. The UNIVAP parameters were fitted and using some literature data for amines and aromatic hydrocarbons, the parameter-matrix was extended.

Keywords: Heats of vaporization; Group contribution; Isothermal calorimetry; UNIVAP

1 Introduction

Heats of vaporization are often required in chemical engineering, especially for dimensioning of thermal equipment. Unfortunately only a few experimental values for heats of vaporization of pure substances can be found in the literature [1]. In the past, group contribution methods for the calculation of the heat of vaporization were proposed which also required the critical temperature or which could be applied at one temperature only, usually 298.15 K. The UNIVAP group contribution method [2] was created to

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overcome these limitations. This approach can be established physically. During evaporation the electrostatic forces between the molecules, which are caused by the interactions between functional groups, have to be dissolved. Therefore heats of vaporization of pure substances can be predicted over a wide temperature range, when the interaction parameters are known. For this purpose, specific measurements for the enthalpy of vaporization are necessary in order to calculate additional parameters for the model.

This paper describes measurements of ΔH_v of specific alcohols using an isothermal microcalorimeter. A specially designed measuring cell was built and tested with *n*-alkanes and 1-alcohols. The experimental values obtained and further data from the compilation of Majer and Svoboda were for the calculation of new interaction parameters for the UNIVAP model.

2. Experimental

2.1. Materials

The reagents were used without further purification: *n*-octane, *n*-decane, *n*-dodecane (Merck), purity >99%; *1*-propanol, *1*-butanol (Merck), purity >99.5%; *1*-heptanol (Merck), 1-decanol (Bayer), purity >99%; 3-buten-1-ol, 1-penten-3-ol, 5-hexen-1-ol (Aldrich), purity >99%; 2,2-dimethyl-3-pentanol, 2,4,4-trimethyl-1-pentanol (Aldrich), purity >98%; 3,3-dimethyl-1-butanol (Aldrich), purity >99%.

2.2. Calorimeter

An isothermal microcalorimeter SETARAM BT 2.15 with a newly designed cell was used. The cell consisted of a cylindrical body with an outer diameter of 17 mm and a length of 80 mm. The correct value for the enthalpy of vaporization can be measured if the liquid and the vapor phase are in thermal equilibrium. For this purpose, it is necessary to ensure a very slow evaporation. Therefore a plate made of brass or a foil made of aluminum with a hole was installed horizontally at the top of the cell. The diameter of the hole varied with the dimensions of the molecules in a range from 0.1 to 1.5 mm. The small size of the hole was necessary in order to obtain a steady slow evaporation, due to the diffusion of the molecules to the outside. The cell was connected with the experimental setup by an electrically heated pipe, which led the vapor to the outside without condensation. To prevent evaporation during temperature regulation, the cell can be set on overpressure with nitrogen up to 0.2–1.5 MPa. The pressure must be reduced during the measurement with a vacuum pump. Two valves (one computer controlled) were used to obtain a slow pressure drop during the whole measurement. The vapor can be absorbed into a washing bottle outside the vacuum pump. The experimental values were corrected with measurements with an unfilled cell. For the calibration of the calorimeter an electrical calibration and reference evaporation with water (bidest) were performed. The method was tested at an average temperature of 338.41 K with *n*-alkanes and *1*-alcohols. For a comparison of the experimental results, literature data were taken at the normal boiling point and converted to 338.41 K with the Watson equation using an exponent of

Table 1

Comparison of experimental and calculated data

Substance	$\Delta H_{v(exp.)}/(kJ\ mol^{-1})$	$\Delta H_{v(calc.)}/(kJ\ mol^{-1})$	Deviation in %
n-Octane	38.64	38.82	–0.46
n-Decane	48.69	48.78	–0.20
n-Dodecane	58.16	57.80	+0.62
1-Propanol	44.38	44.48	–0.24
1-Butanol	48.96	49.04	–0.17
1-Heptanol	63.48	63.64	–0.25
1-Decanol	76.28	76.72	–0.57

0.38. The experimental results show good agreement with the calculated values (Table 1).

3. Results

The experimental results at different temperatures are shown in Table 2. The number of experiments for one alcohol is usually below five. Therefore the maximum deviation of the average value is presented as a measure for the scatter. As the experimental results show, the scatter decreases with increasing temperature. This can be attributed to low vapor pressures of the substances at low temperatures.

Table 2

Experimental results for ΔH_v

Substance	T/K	$\Delta H_v/(kJ\ mol^{-1})$	Deviation in %
3-Buten-1-ol	313.15	50.86	0.39
	327.56	48.81	0.18
	342.79	46.69	0.13
1-Penten-3-ol	313.15	49.85	0.64
	327.56	48.35	0.50
	342.79	46.78	0.19
5-Hexen-1-ol	327.56	60.16	0.15
	342.79	58.00	0.36
	357.93	55.66	0.16
3,3-Dimethyl-1-butanol	327.56	58.64	0.44
	342.79	55.44	0.11
	357.93	52.37	0.002
2,4,4-Trimethyl-1-pentanol	327.69	60.60	0.017
	342.81	58.62	0.085
	357.96	56.54	0.018
2,2-Dimethyl-3-pentanol	327.69	51.78	0.44
	342.81	48.84	0.041
	357.96	45.74	0.26

In this case the vacuum pump is working in the lower threshold region. The experimental values for the enthalpy of vaporization are decreasing almost linearly with increasing temperature (Fig. 1). This is the normal characteristic for such substances in this temperature range. The exponential decrease up to the critical point begins at essentially higher temperatures, usually at $T_r \approx 0.7$.

4. Discussion

The enthalpies of vaporization can be calculated with the UNIVAP model. This model uses parameters describing the electrostatic interactions between groups in the molecule. Therefore it is necessary to calculate the sum over all group enthalpic factors of the different groups k in the molecule of type i:

$$\Delta H_v = R\sum_k \nu_k^{(i)}\varepsilon_k^{(i)} \tag{1}$$

with the group enthalpic factor $\varepsilon_k^{(i)}$:

$$\varepsilon_k^{(i)} = Q_k \left\{ \frac{\sum_m \Theta_m^{(i)}\Psi_{mk})a_{mk} - 2c_{mk}T^2 \exp(c_{mk}T^2) + \exp(c_{mk}T^2)}{\sum_m \Theta_m^{(i)}\Psi_{mk}} \right.$$
$$+\sum_m \left[\Theta_m^{(i)}\Psi_{km} \frac{\left(\sum_p \Theta_p^{(i)}\Psi_{pm}\right)\left(a_{km} - 2c_{km}T^2 \exp(c_{km}T^2) + \exp(c_{km}T^2)\right)}{\left(\sum_p \Theta_p^{(i)}\Psi_{pm}\right)} \right]$$
$$\left. -\sum_m \left[\Theta_m^{(i)}\Psi_{km} \frac{\left(\sum_p \Theta_p^{(i)}\Psi_{pm}\left[a_{pm} - 2c_{pm}T^2 \exp(c_{pm}T^2) + \exp(c_{pm}T^{2)}\right]\right)}{\left(\sum_p \Theta_p^{(i)}\Psi_{pm}\right)^2} \right] \right\} \tag{2}$$

The temperature dependent parameter Ψ_{mk} can be calculated with a modified exponential function:

$$\Psi_{mk} = \exp\left(-\frac{\Delta u_{mk}}{T}\right) \tag{3}$$

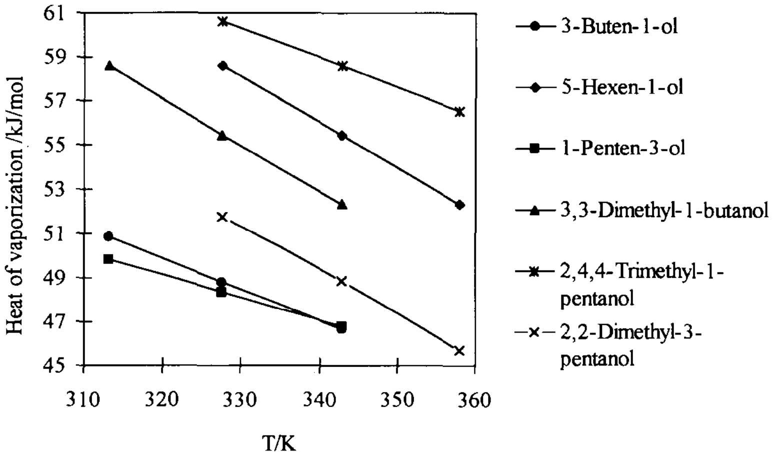


Fig. 1. Heat of vaporization for specific alcohols as a function of temperature.

$$\Delta u_{mk} = a_{mk} + b_{mk}T + \exp(c_{mk}T^2) \tag{4}$$

The surface fraction $\Theta_m^{(i)}$ of group m is defined as:

$$\Theta_m^{(i)} = \frac{v_m^{(i)} Q_m}{\sum\limits_p v_p^{(i)} Q_p} \tag{5}$$

The definition of the groups is shown in Table 3. Despite an earlier paper, some new groups were defined. Especially for aromatics and amines, new main groups were created. Special attention should be paid to the group of the quaternary carbon atom. The group enthalpic factor $\varepsilon_k^{(i)}$ is calculated by totaling all group contributions and then multiplying by the relative van der Waals surface parameter Q_k. The amount of Q_k is zero for a quaternary carbon atom, so that this carbon atom would not make a contribution to the heat of vaporization. Neopentane would then only be constituted by four CH_3 groups, which leads to major errors in ΔH_v prediction. For this reason, the adjacent groups are included. In order to avoid unclarity the following rule applies. If it is not possible to allocate a part of a molecule to one group, it will be incorporated into the group itself as shown in the following example: $(CH_3)_3C{-}CH_2{-}C(CH_3)_3$. This compound is divided in the following manner: 2 $(CH_3)_3C$, 1 CH_2.

Using our experimental data and data from the literature, the parameters for the combinations of main groups m and k were fitted (see Table 4).

Fig. 2 shows the deviation plot of ΔH_v with regard to temperature for different classes of compounds. A systematic deviation cannot be detected. The deviations are very small and agree with previous experience. The parameters were fitted employing the Simplex algorithm [3]. The mean relative deviation (MRD) was used as the error criterion for the fitting procedure:

Table 3
UNIVAP group identifications

	Main group		Subgroup		Surface parameter Q_k
	No.	Name	No.	Name	
Alkanes	1	CH_4	1	CH_4	1.156
	2	CH_3	2	CH_3	0.848
	3	CH_2	3	CH_2	0.540
	4	CH	4	CH	0.228
	5	$(CH_3)_m(CH_2)_n(CH)_1C$	5	$(CH_3)_4C$	3.392
			6	$(CH_3)_3C$	2.544
			7	$(CH_3)_2C$	1.696
			8	$(CH_2)_4C$	2.160
			9	$(CH_2)_3C$	1.852
			9	$(CH_2)_2C$	1.312
			10	$(CH)_4C$	0.912
			11	$(CH)_3C$	0.684
			12	$(CH)_2C$	0.456
			13	$(CH_3)_3(CH_2)C$	3.084
			14	$(CH_3)_2(CH_2)_2C$	2.776
			15	$(CH_3)_3(CH)C$	2.772
			16	$(CH_3)_2(CH)_2C$	2.152
			17	$(CH_2)_3(CH)C$	1.848
			18	$(CH_2)_2(CH)_2C$	1.536
Cyclic alkanes	6	cCH_n	19	cCH_2	0.540
			20	cCH	0.228
Alkenes	7	$CH_n=$	21	$CH_2=$	0.744
			22	CH=	0.432
			23	C=	0.244
			24	=C=	0.343
Alkines	8	$CH_n\equiv$	25	$CH\equiv$	0.696
			26	$C\equiv$	0.392
Alcohols	9	CH_nOH	27	CH_3OH	2.048
			28	CH_2OH	1.740
			29	CHOH	1.428
			30	COH	1.200
Ethers	10	CH_mOCH_n	31	$CH_3(O)CH_3$	1.936
			32	$CH_3(O)CH_2$	1.628
			33	$CH_3(O)CH$	1.316
			34	$CH_3(O)C$	1.088
			35	$CH_2(O)CH_2$	1.320
			36	$CH_2(O)CH$	1.008
			37	$CH_2(O)C$	0.780
			38	CH(O)CH	0.696
			39	CH(O)C	0.468
			40	C(O)C	0.240
Aldehydes	11	CH_nCHO	41	CH_3CHO	1.316
			42	CH_2CHO	1.008
			43	CHCHO	0.696
			44	CCHO	0.468
Ketones	12	CH_mCOCH_n	45	$CH_3(CO)CH_3$	2.336

Table 3 (*continued*)

	Main group		Subgroup		Surface parameter Q_k
	No.	Name	No.	Name	
			46	$CH_3(CO)CH_2$	2.028
			47	$CH_3(CO)CH$	1.716
			48	$CH_3(CO)C$	1.488
			49	$CH_2(CO)CH_2$	1.720
			50	$CH_2(CO)CH$	1.408
			51	$CH_2(CO)C$	1.180
			52	$CH(CO)CH$	1.176
			53	$CH(CO)C$	0.948
			54	$C(CO)C$	0.640
Acids	13	$HCOOH$	55	$HCOOH$	1.532
	14	CH_nCOOH	56	CH_3COOH	2.072
			57	CH_2COOH	1.764
			58	$CHCOOH$	1.452
			59	$CCOOH$	1.224
Esters I	15	$HCOOCH_n$	60	$H(COO)CH_3$	2.036
			61	$H(COO)CH_2$	1.728
			62	$H(COO)CH$	1.416
			63	$H(COO)C$	1.118
Esters II	16	CH_mCOOCH_n	64	$CH_3(COO)CH_3$	2.576
			65	$CH_3(COO)CH_2$	2.268
			66	$CH_3(COO)CH$	1.956
			67	$CH_3(COO)C$	1.728
			68	$CH_2(COO)CH_3$	1.960
			69	$CH_2(COO)CH_2$	1.960
			70	$CH_2(COO)CH$	1.648
			71	$CH_2(COO)C$	1.420
			72	$CH(COO)CH_3$	1.960
			73	$CH(COO)CH_2$	1.960
			74	$CH(COO)CH$	1.340
			75	$CH(COO)C$	1.112
			76	$C(COO)CH_3$	1.960
			77	$C(COO)CH_2$	1.960
			78	$C(COO)CH$	1.960
			79	$C(COO)C$	0.880
Brominated hydrocarbons	17	CH_mBr_n	80	CH_3Br	1.685
			81	CH_2Br	1.376
			82	$CHBr$	1.066
			83	CBr	0.756
			84	CH_2Br_2	2.212
			85	$CHBr_2$	1.902
			86	CBr_2	1.592
			87	$CHBr_3$	2.738
			88	CBr_3	2.429
			89	CBr_4	3.265
Chlorinated hydrocarbons	18	CH_mCl_n	90	CH_3Cl	1.574
			91	CH_2Cl	1.264
			92	$CHCl$	0.952

Table 3 (*continued*)

	Main group		Subgroup		Surface parameter Q_k
	No.	Name	No.	Name	
			93	CCl	0.724
			94	CH_2Cl_2	1.998
			95	$CHCl_2$	1.684
			96	CCl_2	1.448
			97	$CHCl_3$	2.410
			98	CCl_3	2.184
			99	CCl_4	2.910
Chlor-fluorinated hydrocarbons	19	$CH_mCl_nF_t$	100	CH_2ClF	1.760
			101	CHClF	1.450
			102	CClF	1.140
			103	$CHCl_2F$	2.175
			104	CCl_2F	1.865
			105	$CHClF_2$	1.945
			106	$CClF_2$	1.635
			107	CCl_3F	2.591
			108	CCl_2F_2	2.360
			109	$CClF_3$	2.130
Aromatics	20	aCH_n	110	aCH	0.400
			111	aC	0.120
Amines I	21	CH_nNH_2	112	CH_3NH_2	1.544
			113	CH_2NH_2	1.236
			114	$CHNH_2$	0.924
			115	CNH_2	0.696
Amines II	22	CH_mNHCH_n	116	$CH_3(NH)CH_3$	2.092
			117	$CH_3(NH)CH_2$	1.784
			118	$CH_3(NH)CH$	1.472
			119	$CH_3(NH)C$	1.244
			120	$CH_2(NH)CH_2$	1.476
			121	$CH_2(NH)CH$	1.216
			122	$CH_2(NH)C$	0.988
			123	CH(NH)CH	0.904
			124	CH(NH)C	0.676
			125	C(NH)C	0.448

$$\mathrm{MRD} = \frac{\sum_{i=1}^{n} \frac{|\Delta H_{\mathrm{v,calc}} - \Delta H_{\mathrm{v,lit}}|}{\Delta H_{\mathrm{v,lit}}}}{n} \tag{6}$$

A value of less than 1.3% could be estimated. An overview of the actual matrix of fitted parameters is shown in Fig. 3. The black squares mean the parameters were fitted by a large number of data points. For some group combinations, a few data were available in the literature only. These parameters should be used with care and therefore the corresponding squares in the parameter matrix are hatched. Some combinations between main groups are not possible, for example combinations with CH_4.

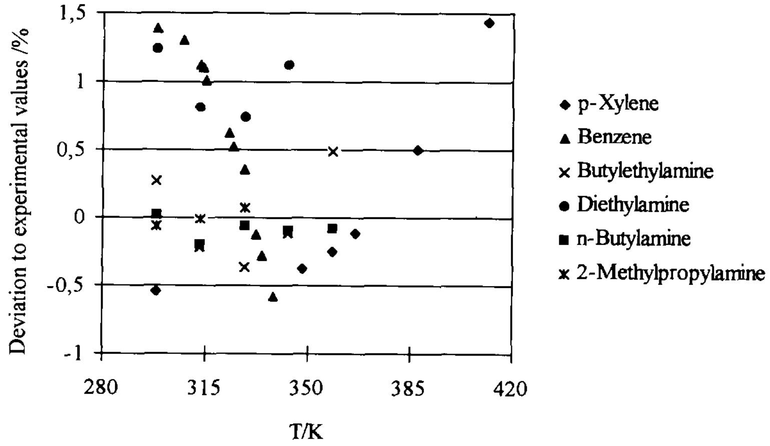
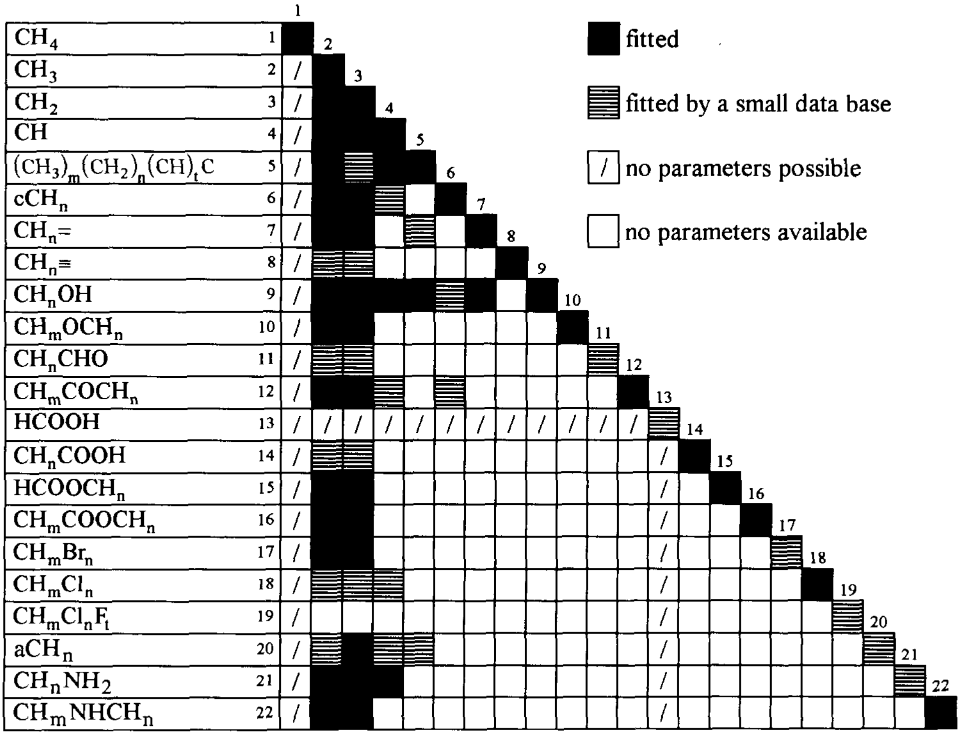


Fig. 2. Deviation plots for the new main groups.



		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
CH_4	1	■																					
CH_3	2	/	■																				
CH_2	3	/	■	■																			
CH	4	/	■	■	■																		
$(CH_3)_m(CH_2)_n(CH)_tC$	5	/	■	▤	■	■																	
cCH_n	6	/	■	■	▤		■																
$CH_n=$	7	/	■	■		▤		■															
$CH_n\equiv$	8	/	▤	▤					■														
CH_nOH	9	/	■	■	■	■	▤	■		■													
CH_mOCH_n	10	/	■	■							■												
CH_nCHO	11	/	▤	▤								▤											
CH_mCOCH_n	12	/	■	■	▤		▤						■										
HCOOH	13	/	/	/	/	/	/	/	/	/	/	/	/	▤									
CH_nCOOH	14	/	▤	▤										/	■								
$HCOOCH_n$	15	/	■	■										/		■							
CH_mCOOCH_n	16	/	■	■										/			■						
CH_mBr_n	17	/	■	■										/				▤					
CH_mCl_n	18	/	▤	▤	▤									/					■				
$CH_mCl_nF_t$	19	/												/						▤			
aCH_n	20	/	▤	■	▤	▤								/							▤		
CH_nNH_2	21	/	■	■	■									/								▤	
CH_mNHCH_n	22	/	■	■										/									■

■ fitted

▤ fitted by a small data base

/ no parameters possible

☐ no parameters available

Fig. 3. UNIVAP parameter matrix.

Table 4

UNIVAP interaction parameters for combinations of the main groups *m* and *k*

m	k	a_{mk}/K	b_{mk}/–	c_{mk}/K^{-2}	a_{km}/K	b_{km}/–	c_{km}/K^{-2}
1	1	2.4302E-2	-1.3589E-2	1.0945E-5			
2	2	0.27689	0.60592	5.0755E-6			
2	3	-0.21565	2.1145E-2	-6.7101E-7	0.18793	-0.10685	-6.8209E-7
2	4	-1.95775	0.59530	-4.8778E-4	1.16215	-3.2709	-9.7207E-4
2	5	-0.10486	7.2788E-3	-5.9808E-7	-0.16111	-0.74353	-2.8966E-6
2	6	0.70118	2.14012	-5.1809E-6	-0.16515	-2.30152	6.0351E-7
2	7	0.41639	6.8172E-3	2.0050E-6	-8.4900E-2	-3.0494	2.8368E-7
2	8	-2.8965	3.5070E-2	-4.9680E-6	0.82361	5.3801E-2	-5.8062E-6
2	9	2.3564	0.12098	-1.2748E-5	0.11201	-1.99942	2.3223E-6
2	10	-1.8151E-2	9.3916E-4	6.6319E-7	-0.23961	-1.8526	-1.0628E-6
2	11	-10.463	-7.5560E-2	-8.5853E-7	10.959	-0.41053	6.3482E-6
2	12	-0.20068	-0.32410	-5.2789E-6	0.48873	-0.64198	-1.8295E-6
2	14	1.9608	0.21311	-4.5389E-4	1.00369	-0.25896	-3.5462E-5
2	15	0.31149	-5.0449E-3	-1.9118E-6	0.36680	1.2220E-2	-9.9411E-6
2	16	-0.38286	-4.1717E-2	2.1633E-6	0.93398	-0.16959	-2.0730E-6
2	17	0.73826	1.2635E-2	-6.8220E-6	0.51846	-3.2061E-2	-2.2126E-6
2	18	1.0129	4.1456E-2	2.3603E-6	-0.70793	0.14086	-8.3655E-7
2	20	7.1419E-5	-2.5965E-3	-8.3760E-6	0.33853	-3.2582	-9.1420E-6
2	21	-39.867	4.5707	-9.9684E-5	1.1413	-2.1239	-3.1452E-5
2	22	1.4318	-4.6666E-2	4.9643E-6	-0.26530	-3.7865	-1.0318E-6
3	3	0.19964	-2.5854E-2	1.4693E-6			
3	4	1.5934	4.4437E-2	-1.5983E-5	-0.54217	-0.77405	-7.8298E-5
3	5	-1.0545	4.8601E-2	-8.6411E-7	2.7932	-0.87579	6.3655E-6
3	6	0.74413	0.24985	1.6247E-6	-0.18494	-0.48763	2.4466E-7
3	7	-0.11350	0.10490	8.0205E-7	0.67106	-2.5646E-2	-1.4679E-6
3	8	0.43936	-0.27839	-3.4049E-6	0.24282	-4.2770E-2	-2.6233E-6
3	9	2.39561	5.3650E-2	-1.6682E-5	-0.87842	0.50702	-1.3097E-5
3	10	0.44540	5.6691E-2	6.7598E-6	0.15585	2.5203E-2	3.3222E-6
3	11	0.37267	-0.13797	7.4949E-6	5.40226	-0.36443	-5.5980E-5
3	12	0.97674	-3.2825E-2	1.9896E-6	0.20941	-8.2440E-2	3.1283E-6
3	14	2.49196	9.0876E-2	4.8898E-6	2.22554	-0.33169	-1.5916E-5
3	15	0.54238	5.5237E-3	-2.6977E-6	0.45638	-1.9689E-2	-1.0323E-5
3	16	2.4651E-2	-1.2105E-2	2.3613E-6	0.71470	-3.4854E-2	1.1904E-6
3	17	0.80712	5.9172E-2	-1.8874E-6	0.67462	-3.2995E-2	4.8155E-6
3	18	0.56304	7.1615E-3	-3.6603E-6	0.55474	0.56610	-2.2441E-5
3	20	0.31893	-0.76099	1.3209E-6	17.794	3.6509	8.8606E-6
3	21	-0.12050	-0.45095	3.2529E-6	5.6373	1.3522	1.0895E-6
3	22	-2.2378	2.9660E-2	3.9145E-6	3.2032	-0.13952	-7.0283E-7
4	4	6.79918	0.16841	-1.0550E-5			
4	5	-0.61521	0.13026	2.7889E-6	-0.61228	3.9974E-2	2.7766E-6
4	6	7.1448E-2	5.2441E-3	-6.4878E-7	7.0394E-2	-2.9722E-3	-4.1328E-7
4	9	-0.69589	3.0084E-2	4.7117E-6	0.13396	-0.10370	-3.7162E-7
4	12	0.26236	-7.7327E-2	4.3128E-6	0.57237	-0.88929	3.8890E-6
4	18	-0.25415	2.5667E-2	7.9758E-6	6.2961E-4	2.6976E-2	-1.8725E-5
4	20	0.13211	2.2003E-2	-9.2877E-6	0.94121	-4.3127	9.2626E-6
4	21	0.33866	7.1382E-3	-6.6736E-6	0.64286	0.11424	-2.2114E-5
5	5	3.5701E-2	-1.6995	2.2097E-6			
5	7	-6.9097	-0.18763	1.4368E-6	9.0121	0.21055	-3.0170E-6

Table 4 (*continued*)

m	k	a_{mk}/K	b_{mk}/–	c_{mk}/K^{-2}	a_{km}/K	b_{km}/–	c_{km}/K^{-2}
5	9	0.52258	–29.323	–5.6094E–5	36.615	2.4558	1.1387E–5
5	20	0.43997	–0.17999	–6.3429E–6	–4.6968E–2	–0.43727	–1.4181E–5
6	6	0.44605	6.1621E–3	1.8399E–6			
6	9	1.9160	–4.7375E–2	2.5590E–6	4.0673	1.6346	–9.7438E–5
6	12	–19.535	–8.4161E–3	–3.8609E–5	26.346	0.16205	–4.8833E–5
7	7	0.33587	–5.3219E–2	6.1545E–6			
7	9	–26.142	1.3169	–5.5592E–6	21.790	0.83753	–5.5197E–5
8	8	0.61398	–2.7894E–2	5.6280E–6			
9	9	1.5352	–1.6187E–2	2.6462E–6			
10	10	0.24592	3.4321E–2	–1.2441E–5			
11	11	1.2432	–2.1133E–2	–1.1460E–5			
12	12	0.50213	–2.5459E–2	–1.1634E–5			
13	13	0.50051	9.6268E–3	–1.8991E–6			
14	14	0.16204	–3.4768E–3	–4.8927E–6			
15	15	0.69027	–1.8061E–2	–1.4530E–5			
16	16	0.40466	–8.0536E–2	–1.1291E–5			
17	17	5.8917E–2	2.6172E–2	–4.0165E–6			
18	18	0.49621	–2.2932E–2	–1.0016E–5			
19	19	0.20189	–1.0947E–2	1.9736E–6			
20	20	1.5499	0.14975	–4.9229E–5			
21	21	3.4375E–2	3.0087E–2	4.7343E–6			
22	22	0.49116	1.8108E–2	–1.3938E–6			

5. Conclusions

With specific measurements for the enthalpy of vaporization, it is possible purposefully to extend the UNIVAP parameter matrix. Due to this fact, special alcohols with three different types of main groups were measured with an isothermal microcalorimeter in the temperature range from 313 to 358 K. The calorimetrically determined heats of vaporization show a scatter of less than 1%. With the fitted parameters of the UNIVAP model, the prediction of the enthalpy of vaporization for pure substances over a wide temperature range is possible with high accuracy, without using the critical temperature. The UNIVAP model shows a mean relative error of less than 1.3%. For the calculation only specific interaction parameters are necessary, due to the structure of the molecule. In the future more experimental work for special group combinations has to be done in order to extend this universal method.

List of symbols

a_{mk}	interaction parameter of the groups m and k (K)
b_{mk}	interaction parameter of the groups m and k
c_{mk}	interaction parameter of the groups m and k (K^{-2})
ΔH_v	enthalpy of vaporization (kJ mol^{-1})

MRD	mean relative deviation (%)
R	universal gas constant (8.31451 J mol^{-1} K^{-1})
T	temperature (K)
T_r	reduced temperature
Δu_{mk}	interaction parameter of the groups m and k (K)

Greek letters

ε_k	group enthalpic factor of group k in the mixture (K)
$\varepsilon_k^{(i)}$	group enthalpic factor of group k in the component i (K)
Ψ_{mk}	interaction parameter of the groups m and k
$\Theta_m^{(i)}$	surface fraction of group m in the component i
$\nu_k^{(i)}$	number of groups of type k in the component i

Subscript

k	group of type k

Appendix A: Example

The enthalpy of vaporization of 3-buten-1-ol shall be calculated at a temperature of 313.15 K. The group specific parameters are given in the following table:

Group name	$\nu_k^{(i)}$	Group number	Main group	Q_m	$\Theta_m^{(i)}$
CH_2	1	3	3	0.540	0.15625
$CH_2=$	1	21	7	0.744	0.21528
$CH=$	1	22	7	0.432	0.12500
CH_2OH	1	28	9	1.740	0.50347

Due to the combinations of main groups the interaction parameters a_{mk}, b_{mk}, c_{mk}, Δu_{mk}, Ψ_{mk} and Y_{mk} are given. Y_{mk} is an abbreviation for the temperature dependent expression:

$$Y_{mk} = a_{mk} - 2c_{mk}T^2 \exp(c_{mk}T^2) + \exp(c_{mk}T^2)$$

m	k	a_{mk}/K	b_{mk}/–	c_{mk}/K^{-2}	Δu_{mk}/K	Ψ_{mk}/–	Y_{mk}/K
3	3	0.19964	–2.5854E–2	1.4692E–6	–6.7416	1.0218	1.0218
3	7	–0.11350	0.10490	8.0205E–7	33.818	0.89763	0.79815
3	9	2.3956	5.3650E–2	–1.6682E–5	20.196	0.93754	3.2277
7	3	0.67106	–2.5650E–2	–1.4679E–6	–6.4953	1.0210	1.7863
7	7	0.33587	–5.3220E–2	6.1545E–6	–14.501	1.0474	–0.04275
7	9	–26.142	1.3169	–5.5592E–6	387.25	0.29037	–24.930
9	3	–0.87842	0.50702	–1.3097E–5	158.17	0.60345	0.10951
9	7	21.790	0.83753	–5.5197E–5	284.07	0.40368	21.843
9	9	1.5352	–1.6190E–2	2.6462E–6	–2.2384	1.0072	2.1587

Eq. (2) can be divided into three terms. The first is defined as the numerator of the first term in Eq. (2). The second is the accompanying denominator. The third expression means the sum of the second and third term in Eq. (2). These three terms have to be calculated for the four different groups k.

k	Numerator	Denominator	Sum	$\varepsilon_k^{(i)}$
1	0.81697	0.81088	0.29425	0.70295
2	4.53611	0.69994	−7.78124	−0.96759
3	4.53611	0.69994	−7.78124	−0.56183
4	−0.89573	0.75238	5.16773	6.92032

With these $\varepsilon_k^{(i)}$ a calculated result of 50.66 kJ mol^{-1} can be obtained. The experimental value is 50.86 kJ mol^{-1}, i.e. a deviation of −0.39% can be found.

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