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SIMPOL.1: a simple group contribution method for predicting vapor pressures and enthalpies of vaporization of multifunctional organic compounds

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Abstract. The SIMPOL.1 group contribution method is developed for predicting the liquid vapor pressure p°_{L} (atm) and enthalpy of vaporization ΔH_{vap} (kJ mol^{-1}) of organic compounds as functions of temperature (T). For each compound i, the method assumes $\log_{10} p^{\circ}_{\mathrm{L},i}(T)=\sum_k \nu_{k,i}\, b_k(T)$ where $\nu_{k,i}$ is the number of groups of type k, and $b_k(T)$ is the contribution to $\log_{10} p^{\circ}_{\mathrm{L},i}(T)$ by each group of type k. A zeroeth group is included that uses $b_0(T)$ with $\nu_{0,i}$=1 for all i. A total of 30 structural groups are considered: molecular carbon, alkyl hydroxyl, aromatic hydroxyl, alkyl ether, alkyl ring ether, aromatic ether, aldehyde, ketone, carboxylic acid, ester, nitrate, nitro, alkyl amine (primary, secondary, and tertiary), aromatic amine, amide (primary, secondary, and tertiary), peroxide, hydroperoxide, peroxy acid, C=C, carbonylperoxynitrate, nitro-phenol, nitro-ester, aromatic rings, non-aromatic rings, C=C–C=O in a non-aromatic ring, and carbon on the acid-side of an amide. The T dependence in each of the $b_k(T)$ is assumed to follow $b(T)=B_1/T+B_2+B_3T+B_4\ln T$. Values of the B coefficients are fit using an initial basis set of 272 compounds for which experimentally based functions $p^{\circ}_{\mathrm{L},i}=f_i(T)$ are available. The range of vapor pressure considered spans fourteen orders of magnitude. The ability of the initially fitted B coefficients to predict p°_{L} values is examined using a test set of 184 compounds and a T range that is as wide as 273.15 to 393.15 K for some compounds. σ_{FIT} is defined as the average over all points of the absolute value of the difference between experimental and predicted values of $\log_{10} p^{\circ}_{\mathrm{L},i}(T)$. After consideration of σ_{FIT} for the test set, the initial basis set and test set compounds are combined, and the B coefficients re-optimized. For all compounds and temperatures, σ_{FIT}=0.34: on average, $p^{\circ}_{\mathrm{L},i}(T)$ values are predicted to within a factor of 2. Because $d(\log_{10} p^{\circ}_{\mathrm{L},i}(T))/d(1/T)$ is related to the enthalpy of vaporization $\Delta H_{\mathrm{vap},i}$, the fitted B provide predictions of $\Delta H_{\mathrm{vap},i}$ based on structure.

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1 Introduction

For organic compound i, knowledge of the liquid vapor pressure $p^{\circ}_{\mathrm{L},i}$ at the system temperature (T) is required whenever phase equilibrium of i between a liquid phase and the gas phase is of interest. This type of partitioning arises frequently in many disciplines, and so the need for reliable $p^{\circ}_{\mathrm{L},i}$ values is considerable. And, since the T dependence of $p^{\circ}_{\mathrm{L},i}$ is determined by the compound-dependent enthalpy of vaporization $\Delta H_{\mathrm{vap},i}$, the same need extends to $\Delta H_{\mathrm{vap},i}$ values. In our case, the topic of interest is gas/particle partitioning in atmospheric and smoke aerosol systems (e.g., Pankow, 1994a, 1994b, 2001, 2003; Pankow et al., 2001, 2003, 2004; Barsanti and Pankow, 2004, 2005, 2006).

Given the infinite structural variety possible with organic compounds, laboratory measurements will never keep pace with the need for new $p^{\circ}_{\mathrm{L},i}$ information. Consequently, there is continuing interest in the development of reliable methods for predicting $p^{\circ}_{\mathrm{L},i}$ and $\Delta H_{\mathrm{vap},i}$ values. In the case of the behavior and formation of organic particulate matter (OPM) in the atmosphere, there is growing interest in a

Table 1a. Non-oxygenated, hydroxyl, ketones, aldehydes, and carboxylic acid saturated compounds in the basis set for the initial fit.

Nonoxygenated alkanes	*Alkanoic ketones and aldehydes*	*Alkanoic carboxylic acids*
2,2-dimethyl pentane	butanal	ethanoic acid
1,1-dimethyl cyclohexane	2-methyl propanal	propanoic acid
cis-1,2-dimethyl-cyclohexane	cylopentanone	2-methyl-propanoic acid
2,2,4 trimethyl pentane	cylohexanone	butanoic acid
	5-methyl-2-hexanone	cyclobutanoic acid
Alkanoic hydroxyls	octanal	3-methyl butanoic acid
cyclobutanol	2-octanone	pentanoic acid
2-butanol	3-hydroxy-3-methyl-2-butanone	cyclopentane carboxylic acid
2-methyl-1-propanol	4-hydroxy-2-pentanone	hexanoic acid
1-butanol	2,4 hexanedione	2-ethyl-butanoic acid
1-pentanol	4-hydroxy-4-methyl-2-pentanone	4-methyl-pentanoic acid
2,2-dimethyl-1-propanol	3-hexanone	cyclohexanecarboxylic acid
2-pentanol	hexanal	heptanoic acid
cyclohexanol	heptanal	octanoic acid
1-hexanol	2-heptanone	nonanoic acid
2-methyl 2-pentanol		2-oxo-propanoic acid
2,3 dimethyl 2-butanol		2-hydroxy-propanoic acid
3-hexanol		4-oxo-pentanoic acid
1,2-propanediol		butanedioic acid
1,4-butanediol		pentanedioic acid
2,3-butanediol		
1,3-butanediol		
1,2-butanediol		
1,5-pentanediol		
2,3-pentanediol		
1,2-pentanediol		
2,4-dimethyl-cyclopentanol		
cycloheptanol		
2-methyl-*cis*-cyclohexanol		

wide range of multi-functional oxygenated compounds and nitrogen-containing compounds, e.g., hydroxy acids, diacids, hydroxy diacids, hydroxy aldehydes, organic nitrates, nitro aldehydes, etc.

Quantum-mechanical calculations are making steady progress in the theater of predicting $p^{\circ}_{\mathrm{L},i}$ values for any structure of interest (Diedenhofen et al., 2007; Verevkin et al., 2007; Banerjee et al., 2006; Tong et al., 2004). However, prediction efforts for more complicated structures can now only be based on either a complex consideration of the interaction forces between molecules (i.e., dispersion, induction, dipole and H-bonding) as in the SPARC model discussed by Hilal et al. (1994), or by empirical group-contribution means.

In the group contribution approach to prediction of molecular properties, it is hypothesized that the value of a property of interest for compound i can be predicted based on empirically determinable contributions from the structural fragments that comprise i. As a function of temperature T, the result is often an equation of the type

$$\log_{10} Z_i(T) = b_0(T) \; + \; \sum\nolimits_k \nu_{k,i}\, b_k(T) \qquad (1)$$

where: $Z_i(T)$is the property of interest, e.g., $p^{\circ}_{\mathrm{L},i}(T)$; the parameter $b_0(T)$ is a T-dependent constant; $\nu_{k,i}$ is the number of groups of type k in i; the index k may take on the values 1,2,3, etc.; and $b_k(T)$ is the group contribution term for group k. Values for $b_0(T)$ and the set of $b_k(T)$ are usually determined by fitting (i.e., optimizing) Eq. (1) using laboratory-based measures of $Z_i(T)$ for a large number of compounds that contain the groups of interest. For example, for both 2,3- and 2,4-dihydroxypentane it can be considered that $\nu_{\mathrm{OH},i}$= 2, $\nu_{\mathrm{CH_3},i}$=2, $\nu_{\mathrm{CH_2},i}$=1, and $\nu_{\mathrm{CH},i}$=2. In this approach, four $b_k(T)$ values are required, and Eq. (1) will give the same prediction for $Z_i(T)$ for both isomers. However, the vicinal nature of the two OH groups in 2,3-dihydroxypentane allows greater intramolecular interaction of the OH groups (and less intermolecular interaction) than in the 2,4 isomer, causing differences in molecular properties. In the case of vapor pressure, $p^{\circ}_{\mathrm{L},i}(T)$ will be higher for the 2,3 isomer than for the 2,4 isomer. Accounting for such property differences among isomers can be accomplished by consideration of additional, "higher-order" groups. Thus, for 2,3-dihydroxypentane a "second-order"

Table 1b. Continued.

Nonoxygenated alkanes		*Nonoxygenated aromatics*
2,3-dimethyl-2-butene		(1,1-dimethyl-ethyl)-benzene
		1,2-diphenyl-ethane
Alkenoic hydroxyls		2-phenyl-propane
3-buten-1-ol	2-methyl-4-penten-2-ol	
3-buten-2-ol	3-cyclohexen-1-ol	*Phenyl alkanoic hydroxyls*
2-methyl-2-buten-1-ol	3-methyl-3-penten-2-ol	1-phenyl-ethanol
2-penten-1-ol	4-methyl-3-penten-1-ol	2-phenyl-ethanol
3-methyl-3-buten-1-ol	cyclohex-1-enyl-methanol	
3-penten-1-ol	3-methyl-2-cyclohexen-1-ol	*Phenols*
2,3-dimethyl-2-buten-1-ol	*cis*-9-octadecen-1-ol	phenol
2-methyl-1-penten-3-ol		2-hydroxy-1-methyl-benzene
Alkenoic ketones and aldehydes		3-hydroxy-1-methyl-benzene
2-butenal	4-methyl-3-penten-2-one	4-hydroxy-1-methyl-benzene
3-buten-2-one	4-methyl-4-penten-2-one	2-ethyl-phenol
2-methyl-2-butenal	5-hexen-2-one	*Aromatic ketones and aldehydes*
3-penten-2-one	5-hexen-3-one	benzaldehyde
2,3-dimethyl-2-butenal	1-cyclohex-1-enyl-ethanone	1-phenyl-ethanone
2,4-hexadienal	3-methyl-3-penten-2-one	2-methyl-benzaldehyde
5-(1-hydroxy-1-methyl-ethyl)-2-methyl-cyclohex-2-enone		2-phenyl-propanal
		1-(2-methyl-phenyl)-ethanone
Alkenoic carboxylic acids		1-phenyl-2-propanone
propenoic-acid	3-hexenoic-acid	*Aromatic carboxylic acids*
2-methyl-propenoic-acid	4-hexenoic-acid	3-methyl-benzoic acid
3-butenoic-acid	2-cyclohexene carboxylic acid	4-methyl-benzoic acid
2-ethyl-propenoic-acid	9,12-octadecadienoic acid	2-phenyl-ethanoic acid
2-pentenoic-acid	9,12,15-octadecatrienoic acid	2-phenyl-propanoic acid
2-cyclopentene-carboxylic-acid		*trans*-3-phenyl-2-propenoic acid

group CH(OH)-CH(OH) (="vicinal-OH") can be invoked with $\nu_{\text{vicinal-OH},i}$=1. Kolská et al. (2005) describe a third-order method for prediction of $\Delta H_{\text{vap},i}$ and the entropy of vaporization $\Delta S_{\text{vap},i}$ values at 298.15 K.

In the most general application of a group contribution model, the fitting takes place over a broad range of compound types, e.g., simple alkanes, functionalized alkanes, aromatics, functionalized aromatics, etc. In that case, $b_0(T)$ serves as a general fitting constant. Alternatively, the fitting can take place within a particular class of compounds, as in the study by Lee et al. (2000) of substituted benzene compounds wherein for predicting $p^{\text{o}}_{\text{L},\,i}(298.15)$ the value of $b_0(298.15)$ was not obtained from the fitting process. Rather, it was defined that $b_0(298.15) = \log_{10} p^{\text{o}}_{\text{L, benzene}}(298.15)$. A second-order group contribution model was then fit to

$$\log_{10} p^{\text{o}}_{\text{L},\,i}(298.15) = \log_{10} p^{\text{o}}_{\text{L, benzene}}(298.15) + \sum_k \nu_{k,i}\, b_k(298.15) \quad (2)$$

The summation accounts for how the presence of the various first- and second-order groups cause $p^{\text{o}}_{\text{L},\,i}(298.15)$ to differ from $p^{\text{o}}_{\text{L, benzene}}(298.15)$.

In a generalization (though first order) of the Lee et al. (2000) approach, Capouet and Müller (2006) allowed that a range of parent structures would be of interest, and so existing $p^{\text{o}}_{\text{L},i}(T)$ data for a range of compounds were fit to

$$\log_{10} p^{\text{o}}_{\text{L},i}(T) \;=\; \log_{10} p^{\text{o}}_{\text{L,hc}-i}(T) \;+\; \sum\nolimits_k \nu_{k,i}\, \tau_k(T) \quad (3)$$

where $p^{\text{o}}_{\text{L,hc}-i}(T)$ is the known vapor pressure for the non-functionalized hydrocarbon (hc) compound that possesses the skeletal structure underlying compound i, and the $\tau_k(T)$ are conceptually equivalent to the $b_k(T)$. Application of Eq. (3) to a particular i requires knowledge (or an independent prediction) of $p^{\text{o}}_{\text{L,hc}-i}(T)$; the summation accounts for how the substituents in i cause $p^{\text{o}}_{\text{L},i}(T)$ to differ from $p^{\text{o}}_{\text{L,hc}-i}(T)$. In the fitting carried out by Capouet and Müller (2006), multiple different hc-i structures were considered; the corresponding $p^{\text{o}}_{\text{L,hc}-i}(T)$ and $p^{\text{o}}_{\text{L},i}(T)$ were taken as the inputs, and the output was a set of $\tau_k(T)$ encompassing 10 groups: OH (as bonded to a primary, secondary, and tertiary carbon); C=O (aldehyde or ketone); COOH; hydroperoxy; nitrate (primary, secondary, and tertiary); and peroxyacetylnitrate (PAN).

Table 1c. Amides, amines, ethers, and nitrate-group containing compounds in the basis set for the initial fit.

Amides		*Ethers*	
formamide	dimethyl-propionamide	1,2-epoxy-3-isopropoxy-propane	1,3-dioxacyclooctane
acetamide	diethyl-formamide	1-butoxy-2-ethoxyethane	1,4-dioxane
methyl-formamide	butyl-acetamide	2,6-dimethoxybenzoic acid	1,3-dioxane
dimethyl-formamide	propanamide	1-(2-methoxyethoxy)-butane	1,1-dimethoxyethene
methyl-acetamide	butyramide	3,4-dimethoxybenzoic acid	1,2-dipropoxyethane
ethyl-formamide	pentanamide	4-methoxy-benzaldehyde	1,3-diethoxypropane
dimethyl-acetamide	hexanamide	2-(2-methylpropoxy)-ethanol	1,1-dimethoxybutane
		3,5-dimethoxybenzoic acid	levoglucosan
Amines		3-(2-methoxyphenyl)-propionic acid	2-*n*-butoxy-1-ethanol
2-propylamine	4-amino-3-methylbenzoic acid	3-(3,4-dimethoxyphenyl)-propionic acid	methoxyethane
1-propylamine	*n*-methyl-*n*-phenyl-amine	5,5-dimethyl-1,3-dioxane	4-methoxy-phenol
phenylamine	dimethyl-hydroxylamine	4,4-dimethyl-1,3-dioxane	1,1-dimethoxy-2-butene
1-pentylamine	1,2,-ethane-diamine	2-methoxy-tetrahydropyran	
4-amino-toluene	3-amino-4-methylbenzoic	3-(4-methoxyphenyl)-propionic acid	
3-amino-toluene	2-methyl-propylamine	*cis*-2,4-dimethyl-1,3-dioxane	
2-amino-toluene	1-methyl-propylamine		
dimethylamine	1-(dimethylamino)-2-propanone	*Nitrates*	
2-butylamine	(1-methyl-ethyl)-methylamine	3-methylbutyl nitrate	
methylamine	*n*-methyl-phenylamine	2-methylpropyl nitrate	
ethylamine	*n*-methyl-1-butanamine	butyl nitrate	
trimethylamine	*n*,*n*-dimethyl-*n*-phenyl-amine	ethyl nitrate	
diethylamine	triethylamine	propylnitrate	
1-butylamine		1-methylethyl nitrate	
		1,2,3-propanetrinitrate	
		cyclopentyl nitrate	

Table 1d. Esters and nitro-group containing compounds in the basis set for the initial fit.

Esters		*Nitro-containing*	
2-methyl-propyl ethanoate	ethyl 2-butoxy-ethanoate	6-methyl-2,4-dinitrophenol	3-nitro-2-pentanol
methyl 3-methyl-butanoate	ethyl 2-propoxy-ethanoate	3-nitro-2-butanol	2-methyl-3-nitrobenzoic
methyl pentanoate	diethyl hexandioanate	1-nitrobutane	3-methyl-2-nitrophenol
ethyl 2-methyl-propanoate	ethyl butanoate	2-nitrobutane	4-methyl-2-nitrophenol
ethyl hexanoate	phenyl-methyl ethanoate	ethyl 2-nitropropionate	5-methyl-2-nitrophenol
hexyl ethanoate	diethyl ethanedioate	methyl 4-nitrobutanoate	4-methoxy-2-nitrophenol
2-methyl-propyl butanoate	methyl cyclopropanoate	1-nitromethyl-1-cyclohexanol	2-nitro-ethanol
methyl heptanoate	ethyl cyclopropanoate	4-(1-methylpropyl)-2-nitrophenol	4-formyl-2-nitrophenol
dibutanoate ethane	propyl pentanoate	2-nitro-1-propanol	4-methyl-3-nitrobenzoic
1-methyl-propyl butanoate	methyl cyclobutanoate	3-nitro-1-propanol	5-methyl-2-nitrobenzoic
propyl 3-methyl-butanoate	ethyl cyclobutanoate	3-methoxy-2-nitrobenzoic	3-nitro-2-butanone
1-methyl-ethyl pentanoate	ethyl cyclopentanoate	4-methoxy-3-nitrobenzoic	ethyl nitroacetate
diethyl cyclopropane-1,1-dicarboxylate	dimethyl 1,2-benzenedicarboxylate	3-methoxy-4-nitrobenzoic	methyl nitroacetate
ethyl 4-methyl-pentanoate	dimethyl 1,3-benzenedicarboxylate	methyl-2-nitropropionate	2-nitrobenzoic acid
2-methyl-propyl 2-methyl-propanoate	dimethyl *cis*-1,3-cyclohexanedicarboxylate	2,4,6-trinitrotoluene	3-nitrobenzoic acid
		2-nitrophenol	4-nitrobenzoic acid

The use of $p^{o}_{L,hc-i}(T)$ in Eq. (3) carries accuracy advantages for predicting $p^{o}_{L,i}(T)$ values because each prediction utilizes important specific knowledge of the vapor pressure of the compound with the underlying hc-*i* structure. It is not surprising, then, that Capouet and Müller (2006) report generally better prediction accuracies for the Eq. (3) method than with the more general UNIFAC-p^{o}_{L} method of Asher et al. (2002), though the fitting constants in Asher et al. (2002) have been superseded by those given in Asher and Pankow (2006). In any case, as a practical matter, requiring knowledge of $p^{o}_{L,hc-i}(T)$ can be a significant disadvantage relative to a more general method that can be executed

Table 1e. Peroxide, hydroperoxide, and carbonylperoxynitrate-group containing compounds in the basis set for the initial fit.

Peroxides	*Carbonylperoxynitrates*
di-*n*-butyl peroxide	peroxyacetylnitrate
di-(1,1-dimethylethyl)-peroxide	
diethyl-peroxide	
Hydroperoxides	*Peroxyacids*
1-methyl-1-phenyl-ethyl-hydroperoxide	1-oxo-ethyl-hydroperoxide
methyl-hydroperoxide	1-oxo-propyl-hydroperoxide
ethyl-hydroperoxide	1-oxo-butyl-hydroperoxide
(1,1-dimethylethyl)-hydroperoxide	

Table 2. Average standard errors for the initial fit for all compounds in the basis set, and by compound class.

Compound class	number of compounds N_c	average absolute error σ_{FIT} log(atm)	average signed error σ_{SGN} log(atm)
All compounds	272	0.29	$-1.4\text{x}10^{-3}$
Alkenes	40	0.27	$-7.0\text{x}10^{-3}$
Amides	14	0.30	$3.6\text{x}10^{-3}$
Amines	27	0.24	$-1.8\text{x}10^{-2}$
Aromatics	21	0.22	$6.2\text{x}10^{-2}$
Carbonylperoxynitrates	1	0.21	$-1.2\text{x}10^{-2}$
Esters	30	0.24	3.0×10^{-2}
Ethers	27	0.21	-7.1×10^{-2}
Hydroperoxides	4	0.20	1.7×10^{-3}
Nitrates	8	0.14	3.2×10^{-2}
Nitro-containing	32	0.41	6.7×10^{-2}
Peroxides	3	0.50	2.8×10^{-2}
Peroxyacids	3	0.18	-1.1×10^{-3}
Saturated	62	0.38	-4.0×10^{-2}

using fitting constants alone, e.g. the method of Asher and Pankow (2006) or that of Makar (2001). Moreover, for the compounds that actually form OPM in the atmosphere, good knowledge of the underlying structures is lacking, the available information being limited to a general idea of structural characteristics such as the number of carbons, the likely number and types of functional groups, and whether any aromatic or non-aromatic rings are likely to be present. The goal of this work was to develop a simple $p^o_{L,i}(T)$ group contribution method for which that level of information would be sufficient.

2 Simplified p^o_L prediction method (SIMPOL.1)

2.1 General

The groups of interest considered include a range of first-order group functionalities important for organic compounds involved in OPM formation, and several second order groups. Nevertheless, the total number of groups N_G was kept as small as possible while still affording good accuracy of the overall fit: SIMPOL.1 is not intended as a method that employs many second- and third-order groups.

The SIMPOL.1 method is based on

$$\log_{10} p^o_{L,i}(T) = b_0(T) + \sum_k \nu_{k,i} b_k(T) \quad \text{k=1, 2, 3, ...} \qquad (4)$$

wherein the role of $b_0(T)$ is the same as in Eq. (1), and the index k may take on the values 1,2,3, etc. The units carried by $p^o_{L,i}(T)$ are atm. The form of Eq. (4) is equivalent to

$$\log_{10} p^o_{L,i}(T) = \nu_{0,i} b_0(T) + \sum_k \nu_{k,i}\, b_k(T) \quad k=1, 2, 3... \qquad (5)$$

so that $b_0(T)$ can be viewed as pertaining to group "zero", with $\nu_{0,i} \equiv 1$ for all i. Thus, Eqs. (4) and (5) are equivalent to

$$\log_{10} p^o_{L,i}(T) \;\; = \;\; \sum_k \nu_{k,i}\, b_k(T) \quad k= 0, 1, 2, 3... \qquad (6)$$

wherein k may take on the values 0,1,2,3, etc., and for k=0, $\nu_{0,i} \equiv 1$ for all i.

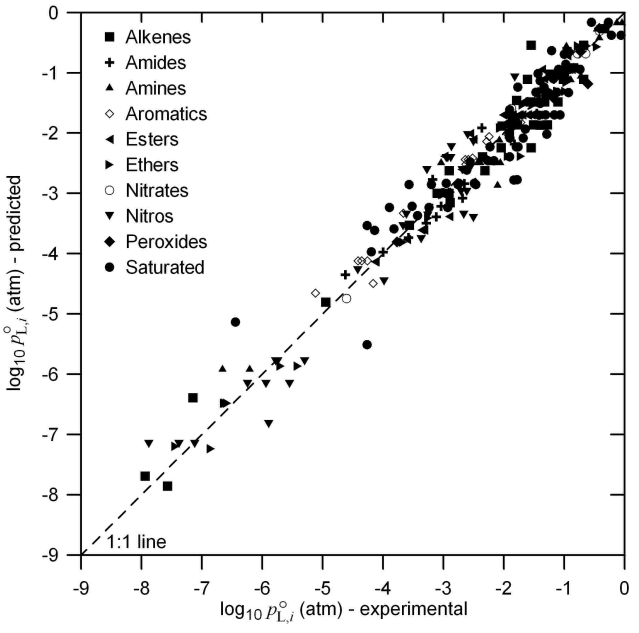

Fig. 1. Predicted vs. experimentally derived $p^{\circ}_{\mathrm{L},i}$ at T=333.15 K for compounds in the initial basis set.

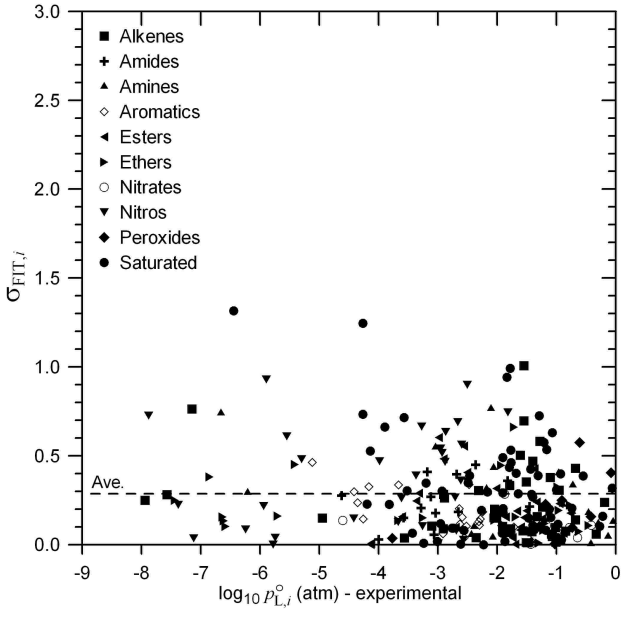

Fig. 2. $\sigma_{\mathrm{FIT},i}$ at 333.15 K for the initial basis set compounds calculated as defined in Eq. (13) plotted vs. the experimentally derived $\log_{10} p^{\circ}_{\mathrm{L},i}(333.15)$.

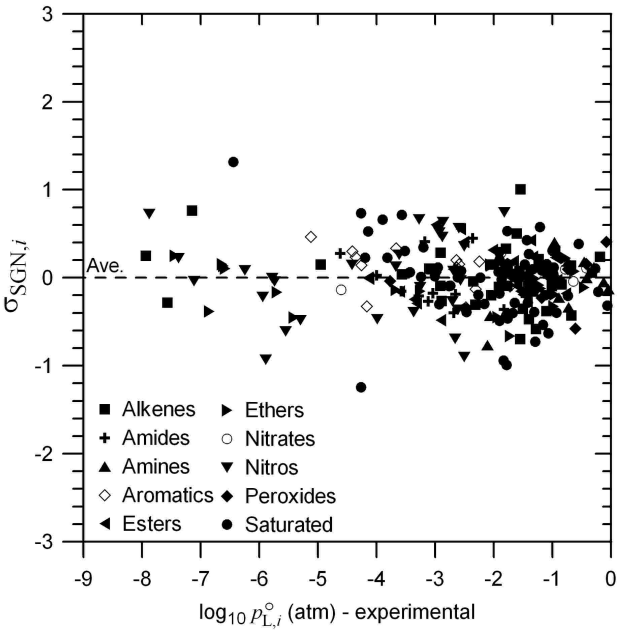

Fig. 3. $\sigma_{\mathrm{SGN},i}$ at 333.15 K for the initial basis set compounds calculated as defined in Eq. (14) plotted vs. experimentally derived $\log_{10} p^{\circ}_{\mathrm{L},i}(333.15)$.

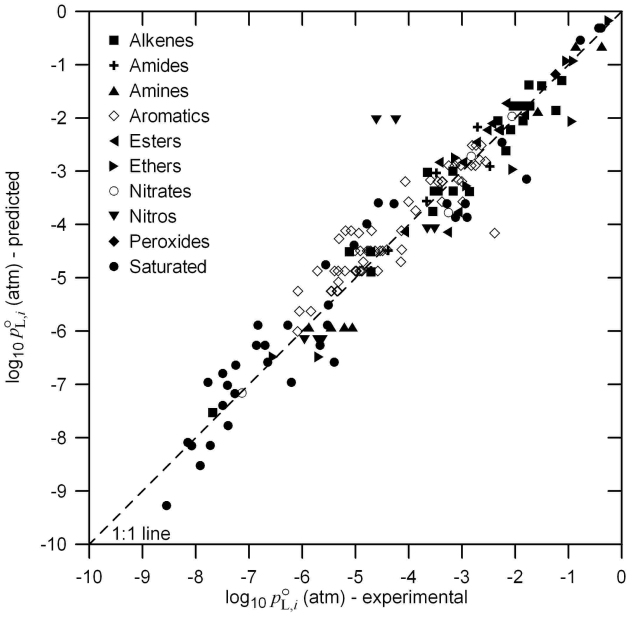

Fig. 4. Predicted vs. experimentally derived $p^{\circ}_{\mathrm{L},i}$ at T=333.15 K for compounds in the test set. Predicted values are based on the optimization using the initial basis set compounds.

Perhaps the most important chemical group in SIMPOL.1 is molecular carbon, for which k=1. Thus, $\nu_{1,i}$ denotes the number of carbon atoms in i, and $b_1(T)$ denotes the per-carbon group contribution to $\log_{10} p^{\circ}_{\mathrm{L},i}(T)$. At ambient temperatures, $b_1(T) \approx -0.5$ (see Table 6 below) and so within any given compound class, $p^{\circ}_{\mathrm{L},i}(T)$ drops by about 1/3 of an order of magnitude for every unit increase in the carbon number.

By way of comparison with prior work from our group, Asher and Pankow (2006) follow Jensen et al. (1981) and

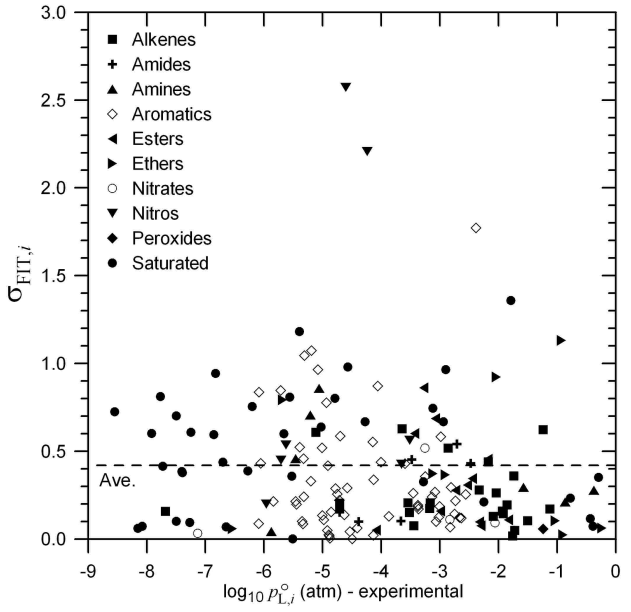

Fig. 5. $\sigma_{\mathrm{FIT},i}$ at 333.15 K for the test set compounds calculated as defined in Eq. (13) plotted vs. experimentally derived $\log_{10} p^{\mathrm{o}}_{\mathrm{L},i}(333.15)$. Predicted $p^{\mathrm{o}}_{\mathrm{L},i}$ values used in calculating the $\sigma_{\mathrm{FIT},i}$ are based on the optimization using the initial basis set compounds.

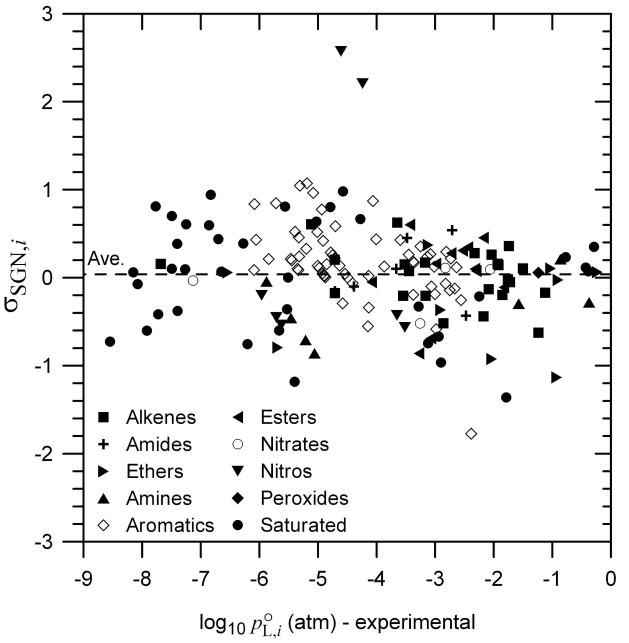

Fig. 6. $\sigma_{\mathrm{SGN},i}$ at 333.15 K for the test set compounds calculated as defined in Eq. (14) plotted vs. experimentally derived $\log_{10} p^{\mathrm{o}}_{\mathrm{L},i}(333.15)$. Predicted $p^{\mathrm{o}}_{\mathrm{L},i}$ values used in calculating the $\sigma_{\mathrm{SGN},i}$ are based on the optimization using the initial basis set compounds.

begin with

$$\log_{10} p^{\mathrm{o}}_{\mathrm{L},i}(T) = \sum\nolimits_k \nu_{k,i} \left[\log_{10}(\Gamma_{k,i}) + \frac{\Delta g_k(T)}{2.303RT} \right] \qquad (7)$$

where: each $\log_{10}(\Gamma_{k,i})$ is a UNIFAC "residual term" that accounts for the intramolecule and intermolecular group-group interactions involving group k; R is the gas constant; and $\Delta g_k(T)$is the difference between the molar free energy of group k in the pure liquid state and in the perfect gas at 1 atm. After using tabulated values of UNIFAC group interactions parameters compiled in Hansen et al. (1991) to compute $\sum_k \nu_{k,i} \log_{10}(\Gamma_{k,i})$ for the compounds in their basis set, Asher and Pankow (2006) fit $p^{\mathrm{o}}_{\mathrm{L},i}(T)$ data values to Eq. (7) to obtain expressions for $\Delta g_k(T)$; a total of 24 groups were considered. Adoption of Eq. (6) in place of Eq. (7) amounts to assuming that each $b_k(T)$ can be fit as a lumped equivalent of $[\log_{10}(\Gamma_{k,i}) + \Delta g_k(T)/2.303RT]$.

In SIMPOL.1, the T dependence in each of the $b_k(T)$ is fit to its own set of $B_{1,k}$ to $B_{4,k}$ according to

$$b_k(T) = \frac{B_{1,k}}{T} + B_{2,k} + B_{3,k}T + B_{4,k} \ln T \qquad (8)$$

which is the form of the T dependence utilized for the 17 coefficients in the UNIFAC model of Jensen et al. (1981). The goal of this work is to use $p^{\mathrm{o}}_{\mathrm{L},i}(T)$ data for a wide range of compounds to obtain best-fit functional representations of the $b_k(T)$.

The temperature dependence of $\log_{10} p^{\mathrm{o}}_{\mathrm{L},i}(T)$ may be used to estimate $\Delta H_{\mathrm{vap},i}(T)$ according to

$$\frac{d \log_{10} p^{\mathrm{o}}_{\mathrm{L},i}(T)}{d(1/T)} = -\frac{\Delta H_{\mathrm{vap},i}(T)}{2.303R} \qquad (9)$$

Thus, by Eq. (6)

$$\Delta H_{\mathrm{vap},i}(T) = -2.303R \sum\nolimits_k \upsilon_{k,i} \frac{d\, b_k(T)}{d(1/T)} \qquad (10)$$

Eq. (10) may be viewed as a group contribution expression for $\Delta H_{\mathrm{vap},i}(T)$ based on the SIMPOL.1 framework where the group contribution to $\Delta H_{\mathrm{vap},i}(T)$, defined as $\Delta h_{\mathrm{vap},i}(T)$, is given by each term in the summation in Eq. (10). Eq. (10) may also be used to derive the predicted change in $\Delta H_{\mathrm{vap},i}(T)$ as a function of T in the SIMPOL.1 framework. Substitution of the functional form for b_k given in Eq. (8) into Eq. (10) and taking the derivative with respect to T results in

$$\frac{d\Delta H_{\mathrm{vap},i}(T)}{dT} = \sum\nolimits_k \upsilon_{k,i} \left[2.303R \left(2B_{3,k}T + B_{4,k} \right) \right] \qquad (11)$$

where the SIMPOL.1 group contribution to $d\Delta H_{\mathrm{vap},i}(T)/dT$ is defined as $d\Delta h_{\mathrm{vap},i}(T)/dT$.

For any real compound i in the liquid state, $\Delta H_{\mathrm{vap},i}(T) > 0$, but $d\Delta H_{\mathrm{vap},i}(T)/dT < 0$ because $\Delta H_{\mathrm{vap},i}$ decreases monotonically to zero as T approaches the compound's critical temperature $T_{c,i}$ (Reid et al., 1986). (As

Table 3a.
Non-oxygenated, hydroxyl, phenolic, aldehyde, ketone, and carboxylic acid compounds in the test set for the initial fit.

Hydroxyls	*Aldehydes and Ketones*	*Carboxylic Acids (cont.)*
2-methyl, 2,4 pentanediol	2-acetyl-cyclopentanone	pinic acid
1,6 hexanediol	2-hydroxy-2-methyl-3-hexanone	norpinic acid
2,3 dimethyl 2,3 butanediol	pinonaldehyde	15-hydroxy-pentadecanoic acid
1,7-heptanediol	caronaldehyde	16-hydroxy-hexadecanoic acid
1,2,3-trihydroxy-propane	5-hexenal	12-hydroxy-octadecanoic acid
4-methyl-4-penten-2-ol	2-cyclohexen-1-one	2-oxo-pentanedioic acid
2-methyl-cyclohex-1-enyl-methanol	5-methyl-5-hexen-2-one	3-oxo-pentanedioic acid
cis-2-butene-1,4-diol	2-ethyl-hex-2-enal	2-oxohexanedioic acid
oct-2-en-4-ol	3,4-dimethyl-hex-3-en-2-one	3-oxohexanedioic acid
3,7-dimethyl-oct-6-en-1-ol	6-methyl-hept-3-en-2-one	5-oxo-nonanedioic acid
5-decen-1-ol	6-methyl-hept-5-en-2-one	5-hexenoic acid
9-decen-1-ol	5-methyl-hept-4-en-3-one	2-octenoic acid
2-phenyl-1-propanol	oct-2-enal	3,7-dimethyl-oct-6-enoic
3-phenyl-1-butanol	3-octen-2-one	2-decenoic acid
1-phenyl-ethanol	2-allyl-2-methyl-cyclopentane-1,3-dione	9-undecenoic acid
1-phenyl-1-propanol	1-phenyl-2-butanone	octadeca-9-enoic acid
1-phenyl-2-propanol	3-phenyl-1-butanal	benzoic acid
3-phenyl-1-propanol	1-(3-methyl-phenyl)-ethanone	2-methyl-benzoic acid
3-phenyl-2-propen-1-ol	1-(4-methyl-phenyl)-ethanone	3-phenyl-propanoic acid
Phenols	1-(2,4-dimethylphenyl)-ethanone	4-phenyl-butanoic acid
3-ethyl-phenol	1-(2-ethyl-phenyl)-ethanone	5-phenyl-pentanoic acid
p-hydroxybiphenyl	1-phenyl-1-propanone	2,3-dimethyl benzoic acid
o-hydroxybiphenyl	1-phenyl-1-butanone	2,4-dimethyl benzoic acid
4-(phenylmethyl)-phenol	4-phenyl-2-butanone	2,5-dimethyl benzoic acid
p-(1,1-dimethylethyl)-phenol	2,4-dimethyl-benzaldehyde	2,6-dimethyl benzoic acid
2-(1,1-dimethylethyl)-4-methylphenol	4-(1-methylethyl)-benzaldehyde	3,4-dimethyl benzoic acid
2-methyl-4-(1,1-dimethylethyl)-phenol	2-hydroxy-benzaldehyde	3,5-dimethyl benzoic acid
5-methyl-2-(1,1-dimethylethyl)-phenol	4-hydroxy-benzaldehyde	2,3,4-trimethyl benzoic acid
2,4,6-tri-(1,1-dimethylethyl)-phenol	*Carboxylic Acids*	2,3,5-trimethyl benzoic acid
1-(4-hydroxyphenyl)-ethanone	2-ethyl-hexanoic acid	2,3,6-trimethyl benzoic acid
1-napthol	propanedioic acid	2,4,5-trimethyl benzoic acid
2-napthol	hexanedioic acid	2,4,6-trimethyl benzoic acid
2-propyl phenol	heptanedioic acid	3,4,5-trimethyl benzoic acid
4-propyl phenol	octanedioic acid	2-(1-methylethyl) benzoic acid
2-(1-methyl-ethyl)-phenol	nonanedioic acid	3-(1-methylethyl) benzoic acid
3-(1-methyl-ethyl)-phenol	decanedioic acid	4-(1-methylethyl) benzoic acid
Saturated Non-oxygenated	undecanedioic acid	2,3,4,5-tetramethyl benzoic acid
cyclohexane	dodecanedioic acid	2,3,4,6-tetramethyl benzoic acid
1,1-dimethyl cyclopentane	3-methyl-hexanedioic acid	2,3,5,6-tetramethyl benzoic acid
trans-1,3-dimethyl cyclopentane	2,2-dimethyl-butanedioic acid	2-(1,1-dimethylethyl) benzoic acid
2,3,4-trimethyl pentane	2-methyl-butanedioic acid	3-(1,1-dimethylethyl) benzoic acid
2,2,3,3-tetramethyl butane	2-methyl-pentanedioic acid	4-(1,1-dimethylethyl) benzoic acid
	2,2-dimethyl-pentanedioic acid	pentamethyl benzoic acid

$T \rightarrow T_{c,i}$, the liquid and gas states for i become increasingly similar, and less and less thermal energy is required for the phase transition.) It is desirable, then, that the values of the fitted parameters used in Eq. (10) yield $d\Delta H_{\mathrm{vap},i}(T)/dT < 0$ with Eq. (11). The extent to which this is observed depends upon the reliability of the $p^{\mathrm{o}}_{\mathrm{L},i}(T)$ data set used in the fitting (including adequate coverage by the data of suitably wide temperature ranges for a mix of compounds that contains all the groups of interest) and the ability of the chosen groups to represent the physical properties of i.

2.2 Fitting the SIMPOL.1 coefficients

All $B_{1,k} - B_{4,k}$ sets were determined by an optimization process using a set of compounds with measured $p^{\mathrm{o}}_{\mathrm{L}}(T)$ values. See Asher et al. (2002) and Asher and Pankow (2006) for descriptions of this type of process. The optimization used nonlinear regression to minimize a least-squares goodness-of-fit criterion defined as

Table 3b. Amide, amine, ester, ether, nitrate, nitro-containing, and peroxide compounds in the test set for the initial fit.

Amides	*Ethers*
heptanamide	4-methyl-1,3-dioxane
octanamide	1,3-dioxepan
methyl-butyramide	1,3-dioxolan
diethyl-butanamide	dimethoxy methane
dimethyl-cyclohexanecarboxamide	*trans*-2,2,4,6-tetramethyl-1,3-dioxane
1-methyl-piperidin-2-one	2-(2-methoxyethoxy)-tetrahydropyran
	(phenoxymethyl)-oxirane
Amines	2-phenyl-1,3-dioxolane
1-amino-2,6-dimethylbenzene	2,3-dimethoxybenzoic acid
n-ethyl-*n*-phenylamine	2,4-dimethoxybenzoic acid
1-amino-2,4-dimethylbenzene	
1-amino-4-ethylbenzene	*Nitrates*
triethanolamine	cyclohexane nitrate
dibutylamine	phenylmethyl nitrate
hexylamine	2,2'-oxybis-ethanol dinitrate
n-propyl-1-propanamine,	2-nitro-2-[(nitrooxy)methyl]-1,3-propanediol dinitrate
n-(1-methylethyl)-2-propanamine	
1-(diethylamino)-2-propanone	*Nitros*
2-amino-3-methylbenzoic	2,4-dinitrophenol
2-amino-5-methylbenzoic	2,5-dinitrophenol
2-amino-6-methylbenzoic	3-nitrophenol
3-amino-2-methylbenzoic	4-nitrophenol
	2-methyl-6-nitrobenzoic acid
Esters	3-methyl-2-nitrobenzoic acid
dimethyl 1,4-benzenedicarboxylate	3-methyl-4-nitrobenzoic acid
methyl dimethoxyethanoate	
diethyl 1,1-cyclopentanedicarboxylate	*Peroxides*
dimethyl propanedioate	di-(1-methyl-propyl) peroxide
1,2-ethanediol diacetate	
methyl benzoate	
phenyl acetate	
ethyl benzoate	
diethyl 1,1-cyclobutanedicarboxylate	
n-propyl benzoate	
2-methyl-propyl benzoate	
n-butyl benzoate	

$$\chi^2 = \sum_{i=1}^{N_c} \sum_{j=1}^{N_{T,i}} \left(\log_{10} \left(p^o_{L,i}(T_{j,i}) \right)_E - \left[b_0 \left(T_{j,i} \right) + \sum_{k=1}^{N_G} \nu_{k,i} b_k \left(T_{j,i} \right) \right] \right)^2 \quad (12)$$

where: N_c is the number of compounds (=272 for the initial basis set); N_G is the total number of groups considered; and each $(p^o_{L,i}(T_{j,i}))_E$ is the vapor pressure of i at temperature T as evaluated using a $p^o_{L,i}=f_i(T)$ expression (e.g., an Antoine-type equation) fitted to experimentally derived $p^o_{L,i}$ data. The $f_i(T)$ expressions used and the associated references are provided in the supplementary online materials http://www.atmos-chem-phys.net/8/2773/2008/acp-8-2773-2008-supplement.pdf. The optimizations were performed using $T_{j,i}$ that could take on the discrete values of 273.15, 293.15, … 393.15 K with all $p^o_{L,i}$ calculated in units of atmospheres. For compounds for which $f_i(T)$ had been fit over that entire range, $N_{T,i}$=7; for others, $N_{T,i}$<7. With the initial basis set compounds, the total number of points considered in the optimization was N=1844.

2.3 Groups and initial basis set compounds

In addition to the zeroeth group, 30 structural groups are considered, giving the total number of groups N_G=31. In addition to molecular carbon (for which k=1), the first-order groups considered are: alkyl hydroxyl, aromatic hydroxyl (e.g., phenol), alkyl ether, alkyl ring ether (e.g, dioxane), aro-

Table 4. Average standard errors in vapor pressures for the test set compounds as estimated by SIMPOL.1 based on the initial basis set compounds in Table 1 and all $T_{j,i}$ for which the experimentally based $p^{o}_{L,i}=f_i(T)$ expressions extended.

Compounds	number of compounds N_c	average absolute error σ_{FIT} log(atm)	average signed error σ_{SGN} log(atm)
All compounds	184	0.45	7.1×10^{-2}
Alkenes	24	0.29	2.8×10^{-2}
Amides	6	0.41	7.1×10^{-2}
Amines	14	0.39	-1.3×10^{-1}
Aromatics	68	0.39	2.0×10^{-1}
Carbonylperoxynitrates	0	n.a.[a]	n.a.[a]
Esters	12	0.36	5.7×10^{-2}
Ethers	10	0.42	-2.5×10^{-1}
Hydroperoxides	0	n.a.[a]	n.a.[a]
Nitrates	4	0.29	-1.1×10^{-1}
Nitro-containing	7	1.0	3.8×10^{-1}
Peroxides	1	0.23	2.4×10^{-2}
Peroxyacids	0	n.a.[a]	n.a.[a]
Saturated	38	0.66	2.5×10^{-3}

[a] n.a.=not available

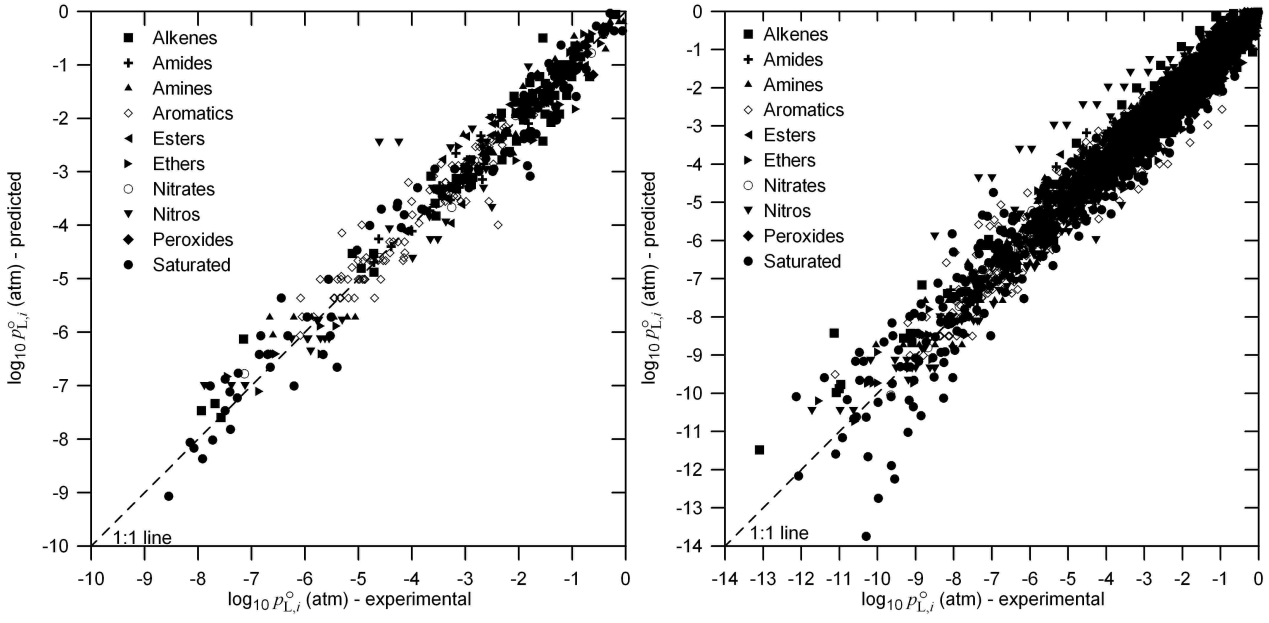

Fig. 7. (a) Predicted vs. experimentally derived $p^{o}_{L,i}$ at T=333.15 K for all compounds based on the final optimization using all of the compounds.
(b) Predicted vs. experimentally derived $p^{o}_{L,i}$ at all seven temperatures for all compounds based on the final optimization using all of the compounds to show the complete data range.

matic ether (e.g., methoxybenzene), aldehyde, ketone, carboxylic acid, ester, nitrate, nitro, alkyl amine (primary, secondary, and tertiary), aromatic amine (e.g., aniline), amide (primary, secondary, and tertiary), peroxide, hydroperoxide, peroxy acid, C=C, and carbonylperoxynitrate. The second-order groups considered are: carbon on the acid-side of an amide for which k=2 (e.g., for n-propyl-butyramide, ν_1=7 and ν_2 = 4); nitro-phenol (as in 2-nitro-phenol), nitro-ester (as in methyl nitroacetate), aromatic rings, non-aromatic rings (as in cyclohexane), and C=C–C=O in a non-aromatic

Table 5. Chemical groups used in SIMPOL.1 and the B values obtained by least-squares optimization using the final fitting set (all compounds in Tables 1 and 3) and giving χ^2=728. Coefficient set predicts $p^o_{L,i}$ in atmospheres.

groups	k	coefficient	footnote comment	$B_{k,1}$	$B_{k,2}$	$B_{k,3}$	$B_{k,4}$
zeroeth group (constant term)	0	b_0	[a]	–4.26938E+02	2.89223E-01	4.42057E-03	2.92846E-01
carbon number	1	b_1	[b]	–4.11248E+02	8.96919E-01	–2.48607E-03	1.40312E-01
carbon number on the acid-side of an amide (asa)	2	b_2	[c]	–1.46442E+02	1.54528E+00	1.71021E-03	–2.78291E-01
aromatic ring	3	b_3	[d]	3.50262E+01	–9.20839E-01	2.24399E-03	–9.36300E-02
non-aromatic ring	4	b_4	[e]	–8.72770E+01	1.78059E+00	–3.07187E-03	–1.04341E-01
C=C (non-aromatic)	5	b_5	[f]	5.73335E+00	1.69764E-02	–6.28957E-04	7.55434E-03
C=C–C=O in non-aromatic ring	6	b_6	[g]	–2.61268E+02	–7.63282E-01	–1.68213E-03	2.89038E-01
hydroxyl (alkyl)	7	b_7	[h]	–7.25373E+02	8.26326E-01	2.50957E-03	–2.32304E-01
aldehyde	8	b_8	[i]	–7.29501E+02	9.86017E-01	–2.92664E-03	1.78077E-01
ketone	9	b_9	[j]	–1.37456E+01	5.23486E-01	5.50298E-04	–2.76950E-01
carboxylic acid	10	b_{10}	[k]	–7.98796E+02	–1.09436E+00	5.24132E-03	–2.28040E-01
ester	11	b_{11}	[L]	–3.93345E+02	–9.51778E-01	–2.19071E-03	3.05843E-01
ether	12	b_{12}	[m]	–1.44334E+02	–1.85617E+00	–2.37491E-05	2.88290E-01
ether (alicyclic)	13	b_{13}	[m]	4.05265E+01	–2.43780E+00	3.60133E-03	9.86422E-02
ether, aromatic	14	b_{14}	[m]	–7.07406E+01	–1.06674E+00	3.73104E-03	–1.44003E-01
nitrate	15	b_{15}	[n]	–7.83648E+02	–1.03439E+00	–1.07148E-03	3.15535E-01
nitro	16	b_{16}	[o]	–5.63872E+02	–7.18416E-01	2.63016E-03	–4.99470E-02
aromatic hydroxyl (e.g., phenol)	17	b_{17}	[p]	–4.53961E+02	–3.26105E-01	–1.39780E-04	–3.93916E-02
amine, primary	18	b_{18}	[q]	3.71375E+01	–2.66753E+00	1.01483E-03	2.14233E-01
amine, secondary	19	b_{19}	[q]	–5.03710E+02	1.04092E+00	–4.12746E-03	1.82790E-01
amine, tertiary	20	b_{20}	[q]	–3.59763E+01	–4.08458E-01	1.67264E-03	–9.98919E-02
amine, aromatic	21	b_{21}	[q]	–6.09432E+02	1.50436E+00	–9.09024E-04	–1.35495E-01
amide, primary	22	b_{22}	[c]	–1.02367E+02	–7.16253E-01	–2.90670E-04	–5.88556E-01
amide, secondary	23	b_{23}	[c]	–1.93802E+03	6.48262E-01	1.73245E-03	3.47940E-02
amide, tertiary	24	b_{24}	[c]	–5.26919E+00	3.06435E-01	3.25397E-03	–6.81506E-01
carbonylperoxynitrate	25	b_{25}	[r]	–2.84042E+02	–6.25424E-01	–8.22474E-04	–8.80549E-02
peroxide	26	b_{26}	[r]	1.50093E+02	2.39875E-02	–3.37969E-03	1.52789E-02
hydroperoxide	27	b_{27}	[r]	–2.03387E+01	–5.48718E+00	8.39075E-03	1.07884E-01
carbonylperoxyacid	28	b_{28}	[r]	–8.38064E+02	–1.09600E+00	–4.24385E-04	2.81812E-01
nitrophenol	29	b_{29}	[p]	–5.27934E+01	–4.63689E-01	–5.11647E-03	3.84965E-01
nitroester	30	b_{30}	[L]	–1.61520E+03	9.01669E-01	1.44536E-03	2.66889E-01

[a] Use for all compounds i with $\upsilon_{0,i}$=1.

[b] Use for all compounds i with $\upsilon_{1,i}$=total number of carbons in the molecule.

[c] If the compound is an amide, use both b_1 and b_2. Examples: for acetamide, use b_0, b_1, b_2, and b_{22}, for methyl acetamide, use b_0, b_1, b_2, and b_{23}, for methyl ethyl acetamide, use b_0, b_1, b_2, and b_{24}.

[d] Use with total number of aromatic rings in a molecule. Examples: for biphenyl, use b_0, b_1, and b_3 with b_3=2; for anthracene, use b_0, b_1, and b_3 with b_3=3.

[e] Use with total number of non-aromatic rings in a molecule. Examples: for cyclohexane, use b_0, b_1, and b_4 with b_4=1.

[f] Use with total number of non-aromatic C=C bonds. Example: for 1-hexene, use b_0, b_1, and b_5 with b_5=1.

[g] Use with total number of C=C–C=O groups in non-aromatic rings. Example: for cyclohex-2-eneone, use b_0, b_1, b_4, b_5, b_6, and b_9 with b_4, b_5, b_6, and b_9 all equal to 1.

[h] Use with total number of hydroxyl groups attached to non-aromatic carbons.

[i] Use with total number of aldehyde groups.

[j] Use with total number of ketone groups.

[k] Use with total number of carboxylic acid groups.

[L] Use with total number of ester groups unless there is a nitro bonded to the acid side carbon chain of the ester, in this case use b_{30}. Examples: for methyl acetate, use b_0, b_1, and b_{11}; for methyl nitroacetate, use b_0, b_1, b_{16}, and b_{30}.

[m] Use with ether groups. If both carbons bonded to the oxygen are not part of an aromatic ring, use b_{12}. If the oxygen is within a non-aromatic ring use b_{13}. Otherwise, use b_{14}. Examples for dimethylether, use b_0, b_1, and b_{12}; for tetrahydrofuran,useb_0, b_1, b_4, and b_{13}; for methylphenyl ether,useb_0, b_1, b_3, and b_{14}.

[n] Use with total number of nitrate groups.

[o] Use with total number of nitro groups. Examples: use b_0, b_1, and b_{16} for 2-nitropropane; use b_0, b_1, b_3, and b_{16} for nitrobenzene.

[p] Use with total number of aromatic hydroxyls (i.e., phenolic hydroxyls) unless there is a nitro group bonded to a benzene ring, in which case use b_{29}. Examples: for 2-methylphenol, use b_0, b_1, b_3, and b_{17}; for 2-nitrophenol, use b_0, b_1, b_3, b_{16}, and b_{29}.

[q] Use with amines. If all carbons bonded to the nitrogen are not aromatic, use b_{11} or b_{12} or b_{13}. Otherwise, use b_{14}. Examples: for methylamine use b_0, b_1, and b_{11}; for dimethylamine use b_0, b_1, and b_{12}; for trimethylamine and for N-benzyl-dimethylamine use b_0, b_1, and b_{13}; for phenylamine, for N-methyl-N-phenylamine, and for N,N-dimethyl-N-phenylamine, use b_0, b_1, and b_{14}.

[r] Use with peroxy compounds. Examples: for peroxy propanyl nitrate use b_0, b_1, and b_{25}; for N-propyl-N-butyl peroxide use b_0, b_1, and b_{26}; for N-butyl peroxide use b_0, b_1, and b_{27}; and for peroxyacetic acid use b_0, b_1, and b_{28}.

Table 6. Values at T = 293.15 K of the b_k group contribution terms from this work, the τ group contribution terms from Capouet and Müller (2006), and for each method whether each group value $d\Delta h_{vap}/dT < 0$ at T=293.15 K.

groups	k	coefficient	this work value of b_k T=293.15	this work $\frac{d\Delta h_{vap,k}(T)}{dT} < 0$? T=293.15 K	Capouet and Müller (2006) value of τ_k T=293.15	Capouet and Müller (2006) $\frac{d\Delta h_{vap}(T)}{dT} < 0$? T=293.15 K
zeroeth group (constant term)	0	b_0	1.79	NO	–[a]	–
carbon number	1	b_1	–0.438	YES	–	–
carbon number, acid-side of amide	2	b_2	–0.0338	NO	–	–
number of aromatic rings	3	b_3	–0.675	NO	–	–
number of non-aromatic rings	4	b_4	–0.0104	YES	–	–
C=C (non-aromatic)	5	b_5	–0.105	YES	–	–
C=C–C=O in non-aromatic ring	6	b_6	–0.506	YES	–	–
hydroxyl (alkyl)	7	b_7	–2.23	NO	–2.76, –2.10, –1.49[b]	no
aldehyde	8	b_8	–1.35	YES	–0.91[c]	no
ketone	9	b_9	–0.935	NO		
carboxylic acid	10	b_{10}	–3.58	NO	–3.10	no
ester	11	b_{11}	–1.20	YES	–	–
ether	12	b_{12}	–0.718	NO	–	–
ether (alicyclic)	13	b_{13}	–0.683	NO	–	–
ether, aromatic	14	b_{14}	–1.03	NO	–	–
nitrate	15	b_{15}	–2.23	YES	–2.12, –1.70, –1.30[d]	no
nitro	16	b_{16}	–2.15	NO	–	–
aromatic hydroxyl (e.g., phenol)	17	b_{17}	–2.14	YES	–	–
amine, primary	18	b_{18}	–1.03	NO	–	–
amine, secondary	19	b_{19}	–0.849	YES	–	–
amine, tertiary	20	b_{20}	-0.608	NO	–	–
amine, aromatic	21	b_{21}	–1.61	YES	–	–
amide, primary	22	b_{22}	–4.49	YES	–	–
amide, secondary	23	b_{23}	–5.26	NO	–	–
amide, tertiary	24	b_{24}	-2.63	NO	–	–
carbonylperoxynitrate	25	b_{25}	–2.34	YES	–	–
peroxide	26	b_{26}	–0.368	YES	–	–
hydroperoxide	27	b_{27}	-2.48	NO	–3.17	no
carbonylperoxyacid	28	b_{28}	–2.48	NO	–3.10	no
nitrophenol	29	b_{29}	0.0432	YES	–	–
nitroester	30	b_{30}	–2.67	NO	–	–

[a] Not considered by Capouet and Müller (2006).
[b] Primary, secondary, and tertiary hydroxyl, respectively.
[c] Capouet and Müller (2006) consider only the carbonyl group.
[d] Primary, secondary, and tertiary nitrate group, respectively.

ring (as in cyclohex-2-enone). Group consideration was not extended to ortho, meta, or para positioning on aromatic rings, or to cis/trans positioning for alkenes.

Table 1 lists the 272 basis set compounds used in the initial fit. There were 6 compounds in the set with primary amide functionality, 4 secondary amides, 4 tertiary amides, 12 primary amines, 4 secondary amines, 3 tertiary amines, 9 aromatic amines, 37 esters, 21 ethers, 10 nitrates, 35 nitros, 3 peroxides, 4 hydroperoxides, 3 peroxy acids, 1 carbonylperoxynitrate, 65 hydroxyls, 6 phenols, 14 aldehydes, 27 ketones, 55 carboxylic acids, 16 aromatic ethers, 16 alkyl ring ethers, 8 nitrophenols, and 5 nitroesters. (These numbers sum to more than 272 because many of the compounds in the basis set had more than one functional group.)

2.4 Optimization

There is no general theoretical method for determining whether a local minimum χ^2 value found by optimizing the set of B values for Eq. (1) is the desired global minimum. However, beginning the optimization with a large number of suitably different sets of initial B values provides an equal number of optimized χ^2 values, and selecting the lowest of these local minima provides a measure of confidence that the corresponding optimized B set either is the set for the global minimum, or is nearly as good as the set for the global minimum.

The χ^2 fitting function in Eq. (1) was minimized using the generalized reduced-gradient method (Lasdon et al., 1978) contained in the nonlinear optimization routines LOADNLP and OPTIMIZE from SOLVER.DLL (Frontline Systems, Boulder, Colorado). The optimization was performed in two steps. First, 100 sets of initial B values (with each

Table 7. Average standard errors in predicting experimental vapor pressures using SIMPOL.1 coefficients optimized for all compounds in Tables 1 and 3 and all $T_{j,i}$ for which the experimentally based $p^{o}_{L,i} = f_i(T)$ expressions extended. Units of σ_{FIT} and σ_{SGN} are $\log_{10}$ (atm).

Compounds	number of compounds N_c	average absolute error σ_{FIT}	average signed error σ_{SGN}
All Compounds	456	0.34	–2.3E-04
Alkenes	64	0.32	–8.2E-03
Nonoxygenated	1	0.16	8.9E-02
Hydroxys	17	0.37	–1.7E-01
Cyclic hydroxys	4	0.23	1.2E-02
Dihydroxys	1	0.57	5.7E-01
Aldehydes	7	0.35	2.3E-01
Ketones	13	0.16	1.4E-01
Cyclic ketones	3	0.25	–8.4E-02
Cyclic hydroxyl ketones	1	0.22	–1.4E-01
Carboxylic acids	15	0.41	–7.9E-02
Cyclic carboxylics	2	0.25	–2.2E-01
Amides	20	0.28	1.1E-02
Primary	8	0.28	1.6E-02
Secondary	5	0.22	2.6E-03
Tertiary	6	0.31	–5.4E-02
Cyclic	1	0.40	4.0E-01
Amines	41	0.28	–9.6E-03
Primary	11	0.22	–2.0E-03
Secondary	8	0.25	–7.2E-02
Tertiary	2	0.18	–1.2E-01
Benzoic acids	6	0.50	2.6E-02
Aromatics	11	0.24	8.5E-03
Ketones	2	0.23	–8.2E-02
Trihydroxys	1	0.52	5.2E-01
Aromatics	89	0.32	3.6E-02
Nonoxygenated	3	0.26	–1.3E-01
Hydroxys	8	0.34	1.2E-02
Hydroxy alkenes	1	0.10	–1.0E-01
Phenols	20	0.36	–4.8E-02
Aldehydes	6	0.28	7.9E-02
Ketones	11	0.18	1.0E-01
Carbonyl phenols	3	1.17	2.3E-01
Benzoic acids	31	0.29	8.3E-02
Other carboxylic acids	5	0.16	–1.4E-01
Carboxylic acid alkenes	1	0.33	3.3E-01
Esters	42	0.25	3.0E-02
Monoesters	23	0.23	2.3E-02
Diesters	11	0.27	–4.4E-02
Cyclic esters	6	0.24	6.4E-02
Ether esters	2	0.48	4.1E-01

Table 7. Continued.

Compounds	number of compounds N_c	average absolute error σ_{FIT}	average signed error σ_{SGN}
Ethers	37	0.31	–5.3E-02
Monoethers	1	0.22	–2.1E-01
Diethers	7	0.18	2.2E-03
Alkene diethers	2	0.12	–1.2E-01
Cyclic diethers	11	0.32	–3.5E-02
Hydroxys	2	0.60	–6.0E-01
Trihydroxy cyclics	1	0.66	6.6E-01
Cyclic ethers	2	0.57	4.8E-02
Carboxylic acid aromatics	6	0.29	–5.3E-03
Aromatic aldehydes	1	0.16	–6.2E-02
Phenols	1	0.12	–6.9E-02
Cyclic and aromatic ethers	1	0.21	–2.1E-01
Carbox. acid aromatic diethers	2	0.44	–1.8E-01
Nitrates	12	0.19	–1.6E-02
Saturated	7	0.21	1.4E-01
Cyclic	2	0.35	–3.5E-01
Nitro trinitrates	1	0.13	–1.3E-01
Saturated trinitrates	1	0.13	–1.3E-01
Ethers	1	0.48	4.8E-01
Nitros	39	0.50	7.0E-02
Saturated	2	0.51	4.8E-01
Aromatics	1	0.41	–4.1E-01
Hydroxys	5	0.47	3.6E-01
Cyclic hydroxyls	1	0.31	1.8E-01
Nitrophenols	7	0.68	6.0E-01
Dinitrophenols	3	0.70	–7.0E-01
Nitrophenol ethers	1	1.24	–1.2E+00
Carbonyl nitrophenols	1	0.64	–6.4E-01
Carbonyls	1	0.52	5.2E-01
Esters	5	0.42	1.3E-02
Nitrobenzoic acids	9	0.29	–2.3E-01
Nitrophenol benzoic acids	3	0.54	5.4E-01
Peroxides	12	0.26	3.0E-03
Carbonylperoxynitrates	1	0.15	–5.4E-02
Hydroperoxides	4	0.18	7.9E-03
Peroxides	4	0.41	–1.3E-02
PeroxyAcids	3	0.18	3.7E-02
Saturated	100	0.43	–4.6E-02
Nonoxygenated	4	0.23	1.7E-01
Cyclic nonoxygenated	5	0.22	–2.8E-02
Hydroxys	10	0.22	–1.7E-01
Cyclic hydroxys	5	0.28	–2.8E-01
Dihydroxys	12	0.38	1.9E-01
Trihydroxys	1	0.60	6.0E-01
Aldehydes	5	0.26	–6.2E-02
Cyclic aldehydes	2	0.39	–2.1E-01
Ketones	5	0.24	1.5E-01
Cyclic ketones	3	0.40	3.4E-01
Hydroxy ketones	4	0.81	–8.1E-01
Carboxylic acids	13	0.41	–1.5E-01
Cyclic carboxylic acids	3	0.11	–1.1E-01
Hydroxy carboxylic acids	4	-1.02	–4.3E-01
Carbonyl carboxylic acids	7	0.81	–2.3E-01
Dicarboxylic acids	17	0.51	1.8E-01

Table 8. Average standard errors ($\sigma_{\Delta H}$ and $\sigma_{\Delta H\_SGN}$) and average relative standard errors ($\rho_{\Delta H}$ and $\rho_{\Delta H\_SGN}$) in predicting $\Delta H_{vap,i}$ values at 335.15 K for organic compounds using SIMPOL.1 coefficients as optimized for all compounds in Tables 1 and 3.

Compounds	number of compounds N_c	average absolute error $\sigma_{\Delta H}$ (kJ mol^{-1})	Average relative absolute error $\rho_{\Delta H}$	average signed error $\sigma_{\Delta H\_SGN}$ (kJ mol^{-1})	Average relative signed error $\rho_{\Delta H\_SGN}$
All Compounds	456	8.9	2.7	1.6E-01	8.0E-02
Alkenes	64	6.6	–1.2	1.2E-01	3.4E-03
Nonoxygenated alkenes	1	8.2	8.2	2.9E-01	2.9E-01
Hydroxy alkenes	17	5.9	4.7	1.2E-01	1.1E-01
Cyclic hydroxyl alkenes	4	9.5	–2.9	1.9E-01	–2.5E-03
Dihydroxy alkenes	1	1.7	1.7	2.6E-02	2.6E-02
Aldehyde alkenes	7	6.8	–2.5	1.4E-01	–2.8E-02
Ketone alkenes	13	3.0	–1.7	7.6E-02	–3.4E-02
Cyclic ketone alkenes	3	10.7	–10.7	2.3E-01	–2.3E-01
Cyclic hydroxyl ketone alkenes	1	29.6	–29.6	3.2E-01	–3.2E-01
Carboxylic acid alkenes	15	7.6	–2.7	9.7E-02	–7.8E-03
Cyclic carboxylic alkenes	2	4.8	-4.8	7.1E-02	–7.1E-02
Amides	20	11.8	0.4	1.9E-01	2.9E-03
Primary amides	8	15.9	–6.5	2.6E-01	–1.1E-01
Secondary amides	5	11.3	8.5	1.7E-01	1.4E-01
Tertiary amides	6	7.5	1.6	1.4E-01	1.9E-02
Cyclic amides	1	7.5	7.5	1.4E-01	1.4E-01
Amines	41	6.2	3.4	1.5E-01	1.0E-01
Primary amines	11	4.4	1.3	1.3E-01	6.3E-02
Secondary amines	8	5.5	3.9	1.7E-01	1.4E-01
Tertiary amines	2	11.3	11.3	4.2E-01	4.2E-01
Benzoic acid amines	6	8.1	2.8	1.0E-01	4.5E-02
Aromatic amines	11	7.0	4.7	1.3E-01	1.0E-01
Ketone amines	2	3.7	3.7	9.6E-02	9.6E-02
Trihydroxy amines	1	3.5	–3.5	3.5E-02	–3.5E-02
Aromatics	89	9.3	4.6	1.4E-01	8.7E-02
Nonoxygenated aromatics	3	9.1	7.8	2.0E-01	1.9E-01
Hydroxy aromatics	8	5.6	–1.3	7.7E-02	–6.9E-03
Hydroxy alkene aromatics	1	7.4	7.4	1.2E-01	1.2E-01
Phenols	20	4.2	–0.4	7.0E-02	–5.4E-03
Aldehydes aromatics	6	10.7	1.8	1.7E-01	7.7E-02
Ketone aromatics	11	3.6	–1.5	5.9E-02	–1.9E-02
Carbonyl phenol aromatics	3	8.1	–4.8	1.2E-01	–6.2E-02
Benzoic acids	31	16.7	13.1	2.5E-01	2.2E-01
Carboxylic acid aromatics	5	2.6	1.4	3.5E-02	2.2E-02
Carboxylic acid alkene aromatics	1	3.1	3.1	4.1E-02	4.1E-02
Esters	42	6.9	3.9	1.7E-01	1.2E-01
Monoesters	23	5.5	3.8	1.2E-01	9.3E-02
Diesters	11	6.5	0.7	1.3E-01	3.0E-02
Cyclic esters	6	13.2	13.2	4.4E-01	4.4E-01
Ether esters	2	5.8	-5.6	9.1E-02	–8.6E-02

set containing 31×4 initial values) were populated randomly (though subject to the condition that the absolute value of all four terms on the right-hand side of Eq. (8) were of order unity). The mean and standard deviation of the 100 χ^2 values were 472 and 23, respectively. The smallest of these χ^2 was 372.

In the second step of the optimization, the set of B values giving χ^2=372 was subjected to further refinement by running 100 additional optimizations, varying each B by a random amount, with all variations restricted within ±30%. The mean and standard deviation of the resulting 100 χ^2 values were 332 and 3, respectively. The smallest of the χ^2 was 325. Further attempts to refine the coefficients did not produce any significant decrease in χ^2. When comparing the B set for χ^2 = 372 to the set for χ^2=325, the median absolute difference is 30%.

3 Results

3.1 Fit accuracy of SIMPOL.1 with initial basis set compounds

The overall agreement between the experimental and predicted values can be assessed in terms of an absolute value form of standard error of the fit:

$$\sigma_{FIT}=\frac{1}{N}\sum_{i=1}^{N_c}\sum_{j=1}^{N_{T,i}}\left|\log_{10}(p^o_{L,i}(T_{j,i}))_P-\log_{10}(p^o_{L,i}(T_{j,i}))_E\right|$$

$$=\frac{1}{N}\sum_{i=1}^{N_c}\sum_{j=1}^{N_{T,i}}\sigma_{FIT,i} \quad (13)$$

where $(p^o_{L,i}(T_{j,i}))_P$ is the predicted vapor pressure for i at temperature $T_{j,i}$ by Eq. (6). For the basis set, N_c=272 and N=1844 (see above), and using the set of B giving χ^2=325 yields σ_{FIT}=0.29 (log units): on average, $(p^o_{L,i}(T_{j,i}))_E$ for

Table 8. Continued.

Compounds	number of compounds N_c	average absolute error $\sigma_{\Delta H}$ (kJ mol^{-1})	Average relative absolute error $\rho_{\Delta H}$	average signed error $\sigma_{\Delta H\_SGN}$ (kJ mol^{-1})	Average relative signed error $\rho_{\Delta H\_SGN}$
Ethers	37	7.2	4.5	1.4E-01	1.1E-01
Monoethers	1	11.3	11.3	4.3E-01	4.3E-01
Diethers	7	3.5	2.6	9.7E-02	8.2E-02
Alkene diethers	2	3.5	3.5	9.4E-02	9.4E-02
Cyclic diethers	11	6.1	5.2	1.5E-01	1.4E-01
Hydroxy ethers	2	12.9	12.9	2.6E-01	2.6E-01
Trihydroxy cyclic ethers	1	21.5	–21.5	1.8E-01	–1.8E-01
Ether cyclic ethers	2	10.5	–2.4	1.8E-01	–1.9E-03
Carboxylic acid aromatic ethers	6	5.0	4.6	6.0E-02	5.6E-02
Aromatic aldehyde ethers	1	10.0	10.0	1.7E-01	1.7E-01
Phenolic ethers	1	7.4	–7.4	1.0E-01	–1.0E-01
Cyclic ether and aromatic ethers	1	9.7	9.7	1.8E-01	1.8E-01
Carboxylic acid aromatic diethers	2	16.0	16.0	2.0E-01	2.0E-01
Nitrates	12	9.2	2.04	1.7E-01	7.7E-02
Saturated nitrates	7	4.4	–0.5	1.2E-01	7.4E-03
Cyclic nitrates	2	7.0	7.0	2.5E-01	2.5E-01
Nitro trinitrates	1	2.4	2.4	8.9E-02	8.9E-02
Saturated trinitrates	1	1.0	1.0	4.1E-02	4.1E-02
Nitrate ethers	1	6.5	-6.5	1.2E-01	–1.2E-01
Nitros	39	11.0	4.2	1.6E-01	7.2E-02
Saturated nitros	2	7.4	2.3	1.7E-01	7.5E-02
Aromatic nitros	1	10.9	10.9	1.3E-01	1.3E-01
Hydroxy nitros	5	7.9	–1.3	1.2E-01	3.2E-03
Cyclic hydroxy nitros	1	27.0	–27.0	2.7E-01	–2.7E-01
Nitrophenols	7	9.2	–9.2	1.3E-01	–1.3E-01
Dinitrophenols	3	2.0	–2.0	2.7E-02	–2.7E-02
Nitrophenol ethers	1	13.1	13.1	2.6E-01	2.6E-01
Carbonyl nitrophenols	1	3.0	–3.0	4.4E-02	–4.4E-02
Carbonyl nitros	1	4.2	–4.2	7.8E-02	–7.8E-02
Nitro esters	5	23.3	23.3	4.1E-01	4.1E-01
Nitrobenzoic acids	9	11.3	11.3	1.5E-01	1.5E-01
Nitrophenol benzoic acids	3	8.7	8.7	9.6E-02	9.6E-02
Peroxides	12	8.6	–1.6	2.0E-01	2.9E-02
Carbonylperoxynitrates	1	8.6	–8.6	2.3E-01	–2.3E-01
Hydroperoxides	4	10.3	–4.2	1.4E-01	1.4E-03
Peroxides	4	11.1	–0.2	3.6E-01	1.0E-01
PeroxyAcids	3	3.1	2.5	7.0E-02	5.5E-02
Saturated	100	11.0	2.4	2.1E-01	1.1E-01
Nonoxygenated	4	9.6	9.6	2.8E-01	2.8E-01
Cyclic nonoxygenated	5	4.6	4.6	1.4E-01	1.4E-01
Hydroxys	10	6.6	6.6	1.4E-01	1.4E-01
Cyclic hydroxys	5	4.1	3.8	8.5E-02	7.9E-02
Dihydroxys	12	4.1	-1.2	5.6E-02	–9.9E-03
Trihydroxys	1	1.3	–1.3	1.5E-02	–1.5E-02
Aldehydes	5	13.7	13.7	4.6E-01	4.6E-01
Cyclic aldehydes	2	22.7	–22.7	3.0E-01	–3.0E-01
Ketones	5	3.5	-2.7	7.3E-02	–5.3E-02
Cyclic ketones	3	6.2	–2.5	1.7E-01	–3.0E-02
Hydroxy ketones	4	9.6	9.6	2.1E-01	2.1E-01
Carboxylic acids	13	7.0	1.6	1.2E-01	5.6E-02
Cyclic carboxylic acids	3	1.7	–1.6	2.7E-02	–2.6E-02
Hydroxy carboxylic acids	4	54.7	42.0	6.7E-01	6.5E-01
Carbonyl carboxylic acids	7	20.6	–12.1	2.0E-01	–8.1E-02
Dicarboxylic acids	17	15.1	–1.8	2.9E-01	1.3E-01

compounds in the basis set is predicted to within a factor of ∼2. This is evidenced in Fig. 1, which is a plot of $\log_{10}(p^{o}_{L,i}(T_{j,i}))_P$ vs. $\log_{10}(p^{o}_{L,i}(T_{j,i}))_E$ for the initial basis set compounds at 333.15 K, the lowest T to which all of the experimentally based $p^{o}_{L,i}=f_i(T)$ expressions extended. It should be noted that although the minimum $p^{o}_{L,i}$ shown in Fig. 1 is 10^{-9} atm, there were 24 values of $p^{o}_{L,i}$ included in the optimization that were lower than 10^{-9} atm with a minimum $p^{o}_{L,i}$ of 7.90×10^{-14} atm. However, these lower values were for compounds at lower temperatures, where the data is not shown on the figure.

Given the multi-functionality possessed by many of the compounds, the 13 major compound class designations used in the figures are somewhat arbitrary. The "saturated" class for example, includes all compounds lacking double bonds and aromatic rings that are not assigned to another class, and so includes simple alcohols, carbonyls, and acids. Similarly, the nitro class contains compounds having only nitro groups, but also compounds with nitro groups and hydroxyl,

Table 9. Numbers of compounds with $d\Delta H_{\mathrm{vap},i}/dT<0$ at T=333.15.

Class	number of compounds total	N_c $d\Delta H_{\mathrm{vap},i}/dT<0$
All Compounds	456	408
Alkenes	64	63
Nonoxygenated alkenes	1	1
Hydroxy alkenes	17	17
Cyclic hydroxyl alkenes	4	4
Dihydroxy alkenes	1	1
Aldehyde alkenes	7	7
Ketone alkenes	13	13
Cyclic ketone alkenes	3	3
Cyclic hydroxyl ketone alkenes	1	1
Carboxylic acid alkenes	15	14
Cyclic carboxylic alkenes	2	2
Amides	20	12
Primary amides	8	6
Secondary amides	5	1
Tertiary amides	6	4
Cyclic amides	1	1
Amines	41	38
Primary amines	11	8
Secondary amines	8	8
Tertiary amines	2	2
Benzoic acid amines	6	6
Aromatic amines	11	11
Ketone amines	2	2
Trihydroxy amines	1	1
Aromatics	89	89
Nonoxygenated aromatics	3	3
Hydroxy aromatics	8	8
Hydroxy alkene aromatics	1	1
Phenols	20	20
Aldehydes aromatics	6	6
Ketone aromatics	11	11
Carbonyl phenol aromatics	3	3
Benzoic acids	31	31
Carboxylic acid aromatics	5	5
Carboxylic acid alkene aromatics	1	1
Esters	42	42
Monoesters	23	23
Diesters	11	11
Cyclic esters	6	6
Ether esters	2	2

carbonyl, or acid functionality. Table 2 provides σ_{FIT} for the initial basis set by compound class, i.e., with N_c and N in Eq. (13) limited to represent the compounds within a particular class. Figure 2 provides a plot of the corresponding individual $\sigma_{\mathrm{FIT},i}$ vs. $\log_{10}(p^{\mathrm{o}}_{\mathrm{L},i}(T_{j,i}))_{\mathrm{E}}$ for 333.15 K.

An estimate of the method bias towards over- or underfitting the $p^{\mathrm{o}}_{\mathrm{L},i}$ is obtained by a variation of Eq. (13) that does not use absolute values:

$$\sigma_{\mathrm{SGN}}=\frac{1}{N}\sum_{i=1}^{N_c}\sum_{j=1}^{N_{\mathrm{T},i}}\left(\log_{10}p^{\mathrm{o}}_{\mathrm{L},i}(T_{j,i})_{\mathrm{P}}-\log_{10}p^{\mathrm{o}}_{\mathrm{L},i}(T_{j,i})_{\mathrm{E}}\right)$$
$$=\frac{1}{N}\sum_{i=1}^{N_c}\sum_{j=1}^{N_{\mathrm{T},i}}\sigma_{\mathrm{SGN},i} \quad (14)$$

Table 9. Continued.

Class	number of compounds total	N_c $d\Delta H_{vap,i}/dT<0$
Ethers	37	36
Monoethers	1	1
Diethers	7	7
Alkene diethers	2	2
Cyclic diethers	11	10
Hydroxy ethers	2	2
Trihydroxy cyclic ethers	1	1
Ether cyclic ethers	2	2
Carboxylic acid aromatic ethers	6	6
Aromatic aldehyde ethers	1	1
Phenolic ethers	1	1
Cyclic ether and aromatic ethers	1	1
Carboxylic acid aromatic diethers	2	2
Nitrates	12	12
Saturated nitrates	7	6
Cyclic nitrates	2	2
Nitro trinitrates	1	0
Saturated trinitrates	1	0
Nitrate ethers	1	1
Nitros	39	32
Saturated nitros	2	2
Aromatic nitros	1	1
Hydroxy nitros	5	1
Cyclic hydroxy nitros	1	1
Nitrophenols	7	7
Dinitrophenols	3	3
Nitrophenol ethers	1	1
Carbonyl nitrophenols	1	1
Carbonyl nitros	1	1
Nitro esters	5	2
Nitrobenzoic acids	9	9
Nitrophenol benzoic acids	3	3
Peroxides	12	8
Carbonylperoxynitrates	1	1
Hydroperoxides	4	1
Peroxides	4	4
PeroxyAcids	3	2
Saturated	100	76
Nonoxygenated	4	4
Cyclic nonoxygenated	5	5
Hydroxy	10	10
Cyclic hydroxy	5	5
Dihydroxy	12	6
Trihydroxy	1	0
Aldehyde	5	5
Cyclic aldehyde	2	2
Ketone	5	5
Cyclic ketone	3	3
Hydroxy ketone	4	4
Carboxylic acid	13	9
Cyclic carboxylic acid	3	3
Hydroxy carboxylic acid	4	3
Carbonyl carboxylic acid	7	2
Dicarboxylic acid	17	10

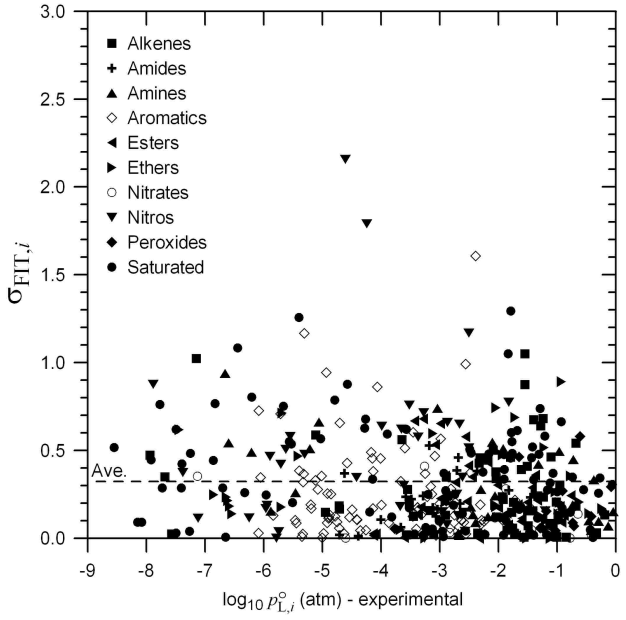

Fig. 8. $\sigma_{\mathrm{FIT},i}$ at 333.15 K for all compounds calculated as defined in Eq. (13) plotted vs. experimentally derived $\log_{10} p^{\mathrm{o}}_{\mathrm{L},i}(333.15)$. Predicted $p^{\mathrm{o}}_{\mathrm{L},i}$ values used in calculating the $\sigma_{\mathrm{FIT},i}$ are based on the final optimization using all of the compounds.

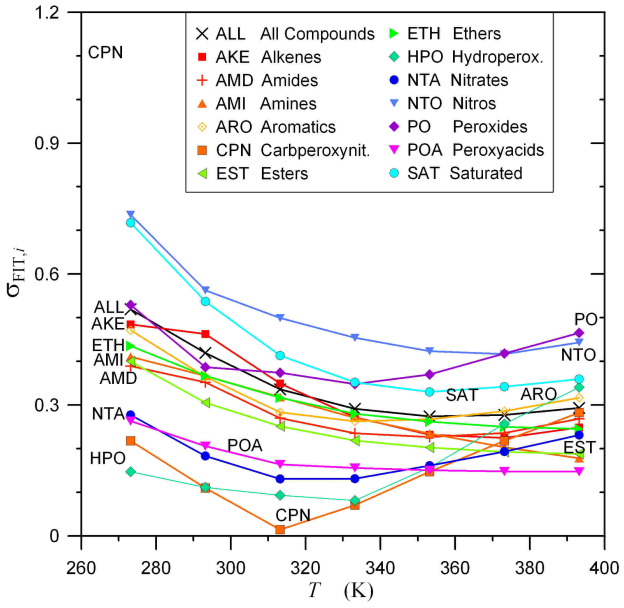

Fig. 10. σ_{FIT} as a function of T and compound class. Predicted $p^{\mathrm{o}}_{\mathrm{L},i}$ values used in calculating the σ_{FIT} are based on the final optimization using all of the compounds.

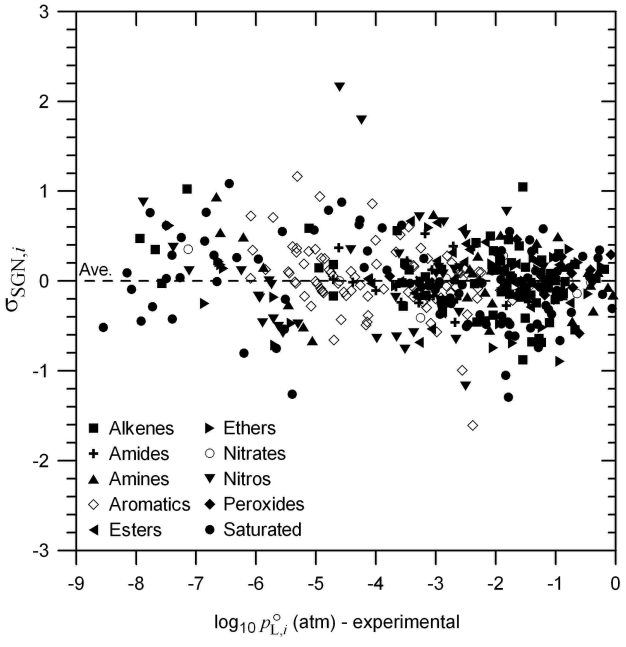

Fig. 9. $\sigma_{\mathrm{SGN},i}$ at 333.15 K for all compounds calculated as defined in Eq. (14) plotted vs. experimentally derived $\log_{10} p^{\mathrm{o}}_{\mathrm{L},i}(333.15)$. Predicted $p^{\mathrm{o}}_{\mathrm{L},i}$ values used in calculating the $\sigma_{\mathrm{SGN},i}$ are based on the final optimization using all of the compounds.

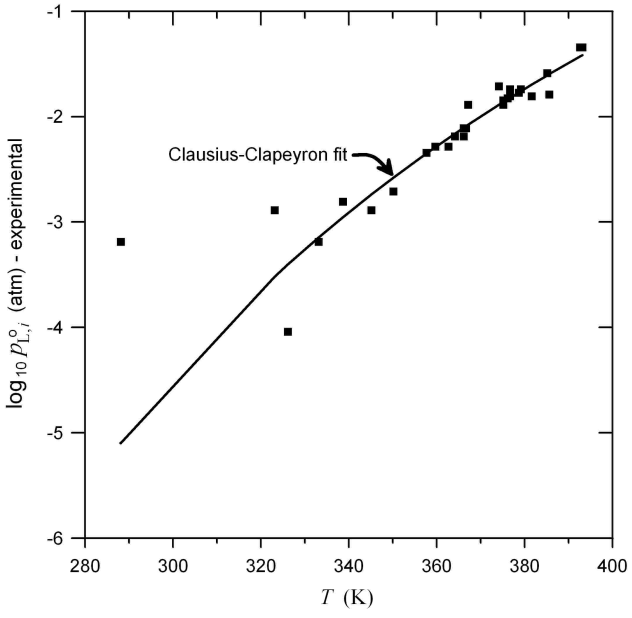

Fig. 11. Experimental $p^{\mathrm{o}}_{\mathrm{L}}$ data for nitroethanol from the Beilstein PlusReactions Database BS070100PR (http://www.beilstein.com/) showing increase in uncertainty in data as temperature decreases. Solid line is fit to the data.

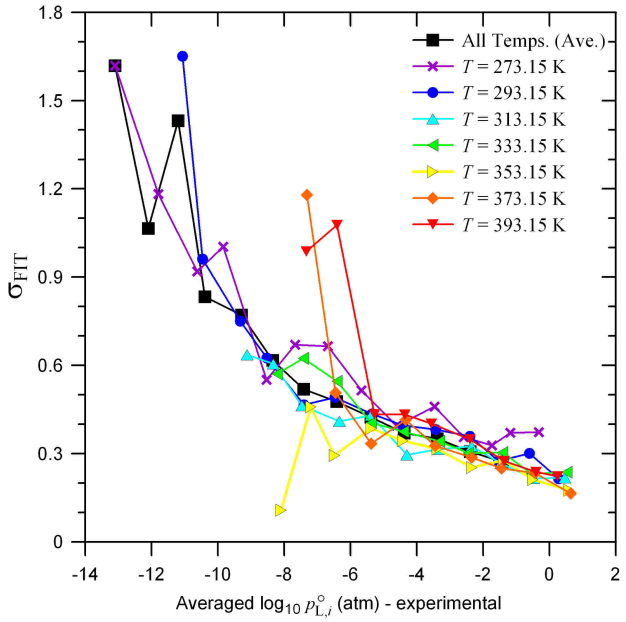

Fig. 12. The standard error σ_{FIT} at each T was calculated by sorting all compounds by increasing $p_{\mathrm{L}}^{\mathrm{o}}$, and then computing the average σ_{FIT} values and $p_{\mathrm{L}}^{\mathrm{o}}$ values over decade ranges. E.g., at 333.15 K, each x-coordinate is the $\log_{10}$ value of the $p_{\mathrm{L}}^{\mathrm{o}}$ average for all compounds with 1×10^{-6} atm$\leq p_{\mathrm{L}}^{\mathrm{o}}<1\times10^{-5}$ atm at that T, and the y-coordinate is the average of the corresponding $\sigma_{\mathrm{FIT},i}$ values.

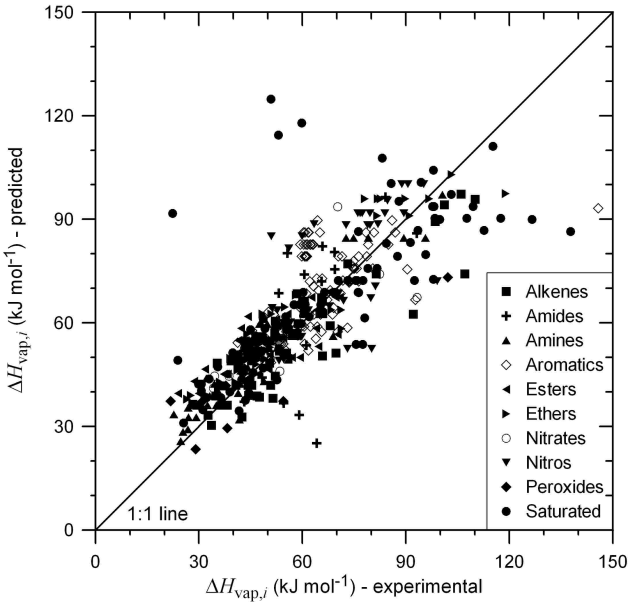

Fig. 13. $\Delta H_{\mathrm{vap},i}$ at 333.15 K based on Eq. (10) and the final coefficients in Table 5, vs. $\Delta H_{\mathrm{vap},i}$ at 333.15 K based on Eq. (9) and the experimentally based $p_{\mathrm{L},i}^{\mathrm{o}}=f_i(T)$ functions.

For the initial basis set of compounds, the set of B producing χ^2=325 gives $\sigma_{\mathrm{SGN}}=1.4\times10^{-3}$ (log units). This indicates that as averaged over all 272 initial basis set compounds and seven temperatures, there is no significant bias in the fitting; the σ_{SGN} values in Table 2 indicate that this result extends down to each of the 13 major compound classes considered. Figure 3 provides a plot of the corresponding individual $\sigma_{\mathrm{SGN},i}$ vs. $\log_{10}(p_{\mathrm{L},i}^{\mathrm{o}}(T_{j,i}))_{\mathrm{E}}$ for 333.15 K.

3.2 Method validation of SIMPOL.1 with a test set of compounds

The ability of the set of B coefficients producing χ^2=325 to predict values of $(p_{\mathrm{L},i}^{\mathrm{o}}(T_{j,i}))_{\mathrm{E}}$ for compounds outside the initial basis set was examined using a test set of 184 compounds (Table 3) with N=1245 $(p_{\mathrm{L},i}^{\mathrm{o}}(T_{j,i}))_{\mathrm{E}}$ values chosen to span the range of volatilities and functionalities of the compounds in the basis set; the results are given in Figs. 4–6 and Table 4. The $p_{\mathrm{L},i}^{\mathrm{o}}=f_i(T)$ expressions used in evaluation of the $(p_{\mathrm{L},i}^{\mathrm{o}}(T_{j,i}))_{\mathrm{E}}$ are provided in the supplementary online materials http://www.atmos-chem-phys.net/8/2773/2008/acp-8-2773-2008-supplement.pdf. Averaged over all test set compounds, σ_{FIT}=0.45, and σ_{SGN}=−0.071: the average prediction error is a factor of ∼3, and there is no significant overall bias. Table 4 gives σ_{FIT} and σ_{SGN} values for the test compounds when N_{c} and N are limited to represent the compounds within a particular compound class. Overall, given the wide range of compounds in the test set, SIMPOL.1 does well in predicting $(p_{\mathrm{L},i}^{\mathrm{o}}(T_{j,i}))_{\mathrm{E}}$. However, the individual compounds for which the performance is appears to be poor bear some discussion. In the case of the nitro class, σ_{FIT} and σ_{SGN} are 1.0 and 0.40, respectively. These ostensibly poor results are driven by: 1) the small number of nitro compounds in the test set; and 2) large apparent errors for only two of the nitro compounds, 3-nitrophenol and 4-nitrophenol ($\sigma_{\mathrm{FIT},i}$=2.64 and 2.24, respectively). The cause of the poor performance for 3-nitrophenol and 4-nitrophenol is not clear. By comparison, for 2-nitrophenol (which is in the initial basis set), $\sigma_{\mathrm{FIT},i}$ is better (0.42). Thus, there might be a large effect of meta and para substitution on $p_{\mathrm{L}}^{\mathrm{o}}$ for nitrophenols. Alternatively, it is possible that the $(p_{\mathrm{L},i}^{\mathrm{o}}(T_{j,i}))_{\mathrm{E}}$ values for 3-nitrophenol and 4-nitrophenol are in error. Indeed, it is undoubtedly true that some of the experimentally based $p_{\mathrm{L},i}^{\mathrm{o}}=f_i(T)$ expressions suffer from significant error: numerous prior parameter prediction studies have identified experimental data that likely are in error, e.g., see the comments by Rathbun (1987) on the likelihood of errors in the $p_{\mathrm{L}}^{\mathrm{o}}$ data of Stull (1947) for 2-pentanone and other similar ketones.

Besides compounds containing the nitro group, method performance appears to be relatively poor for some compounds in the saturated class, the aromatic class, and some compounds in the ether class. For the saturated class, σ_{FIT}=0.66, due mainly to 2-hydroxy-2-methyl-3-hexanone, 2-ethyl-hexanoic acid, norpinic acid, and the three long-chain hydroxyl acids. When these six compounds are removed, σ_{FIT} for the remaining 32 compounds is lowered to

0.51, and the method may be viewed as performing relatively well. Given their relatively simple structures, (i.e., the absence of likely effects from higher order groups), errors in some of the $(p^{\circ}_{\mathrm{L},i}(T_{j,i}))_{\mathrm{E}}$ values for compounds in the saturated class seem possible. This is especially the case for the hydroxyl acids, where at T=273.15 K SIMPOL.1 underestimates the measured $(p^{\circ}_{\mathrm{L},i}(T_{j,i}))_{\mathrm{E}}$ by over 3 orders of magnitude. However, SIMPOL.1 overestimates the measured $(p^{\circ}_{\mathrm{L},i}(T_{j,i}))_{\mathrm{E}}$ by a factor of at least 10 for T=273.15 K, suggesting that the dependence of $(p^{\circ}_{\mathrm{L},i}(T_{j,i}))_{\mathrm{E}}$ on T is very different from that predicted overall by SIMPOL.1. For the ethers, the overall error is relatively low, σ_{FIT}=0.42, with a relatively large bias, σ_{SGN}=−0.25, but there are not consistent patterns in the results that explain the relatively large bias. However, for *trans*-2,2,4,6-tetramethyl-1,3-dioxane, for its set of $T_{j,i}$ values, $\sigma_{\mathrm{FIT},i}$ averages 1.2; removing this compound from the average for the ether class dramatically reduces the magnitudes of σ_{FIT} and σ_{SGN} for the ethers to 0.34 and –0.15, respectively.

3.3 Final coefficients for SIMPOL.1 and associated error estimates for p°_{L} values

In the determination of the final set of B coefficients, the basis set compounds in Table 1 were combined with the test set compounds in Table 3. For this combined set (456 compounds), the set of B coefficients determined using the initial basis set gives χ^2=855. For each of 100 subsequent optimization runs, the initial value of each B coefficient was taken as the final value determined using the initial basis set modified randomly by at most ±30%. The lowest χ^2 value thus obtained was 728 (mean=736, standard deviation=6). Further optimization attempts did not succeed in lowering χ^2.

Table 5 gives the final B coefficients giving χ^2=736. Table 6 gives the values of the $b_k(T)$ at T=293.15: at that T, adding one carbon, carboxylic acid, alkyl hydroxyl, ketone, or aldehyde groups alters $\log_{10} p^{\circ}_{\mathrm{L},i}$ by –0.438, –3.58, –2.23, –0.935, and –1.35, respectively. For comparison, Table 6 also provides the corresponding values of τ_k(293.15) from Capouet and Müller (2006); these are generally similar to the b_k(293.15) determined here. For the carboxylic acid, primary hydroxyl, and carbonyl (i.e., ketone *or* aldehyde) groups, Capouet and Müller (2006) give τ_k(293.15)=–3.10, –2.76, and –0.91.

Consider the transformation of cyclohexene to adipic acid, an example that has historical significance in the evolution of the understanding of the formation of secondary OPM in the atmosphere (Haagen-Smit, 1952). For cyclohexene, υ_0=1, υ_1=6, υ_4=1, and υ_5=1, and by Eq. (6) and the values in Table 6, SIMPOL.1 predicts $\log_{10} p^{\circ}_{\mathrm{L}}$(293.15)=−0.94. For adipic acid, υ_0=1, υ_1=6, and υ_{10}=2, and SIMPOL.1 predicts $\log_{10} p^{\circ}_{\mathrm{L}}$(293.15)=−7.99. Overall, for cyclohexene→adipic acid, the SIMPOL.1 method provides a simple parameterization for quantifying how addition of two COOH groups (b_{10}=−3.58 at 293.15 K) causes a seven order magnitude change in volatility. The $\log_{10} p^{\circ}_{\mathrm{L}}$(293.15) values derived using SIMPOL.1 may be compared with experimental values as follows. For cyclohexene, data in Lister (1941), Meyer and Hotz (1973) and Steele et al. (1996) yield the Antoine fit $\log_{10} p^{\circ}_{\mathrm{L}}(T)$=4.814-(1713/($T$+0.04870)), which gives $\log_{10} p^{\circ}_{\mathrm{L}}(T)$=−1.08 at 293.15 K. For adipic acid, when the $p^{\circ}_{\mathrm{S}}(T)$ (sublimation) data of Davies and Thomas (1960), Tao and McMurray (1989), Chattopadhyay and Zieman (2005), and Cappa et al. (2007) are combined with the entropy of fusion data of Roux et al. (2005) and averaged with sub-cooled liquid vapor pressures from Bilde et al. (2003), the resulting value for $\log_{10} p^{\circ}_{\mathrm{L}}$ is –8.49 at 293.15 K.

Figure 7a provides a plot of $\log_{10}(p^{\circ}_{\mathrm{L},i}(T_{j,i}))_{\mathrm{P}}$ vs. $\log_{10}(p^{\circ}_{\mathrm{L},i}(T_{j,i}))_{\mathrm{E}}$ for all compounds at T=333.15 K and Fig. 7b is a plot of $\log_{10}(p^{\circ}_{\mathrm{L},i}(T_{j,i}))_{\mathrm{P}}$ vs. $\log_{10}(p^{\circ}_{\mathrm{L},i}(T_{j,i}))_{\mathrm{E}}$ for all compounds at all seven temperatures showing the full lower volatility range of the dataset; Figs. 8 and 9 provide corresponding plots of $\sigma_{\mathrm{SGN},i}$ and $\sigma_{\mathrm{FIT},i}$ vs. $\log_{10}(p^{\circ}_{\mathrm{L},i}(T_{j,i}))_{\mathrm{E}}$ except in the interest of brevity the data in Figs. 8 and 9 are shown for T=333.15 K only. Table 7 provides σ_{SGN} and σ_{FIT} values by compound class and sub-class. All σ_{SGN} values for the major classes are low (no significant biases). However, among the compounds containing the nitro group, as noted above, p°_{L} is predicted poorly for 3-nitrophenol and 4-nitrophenol. When these two compounds are excluded, σ_{FIT} for the nitro class is reduced from 0.50 to 0.42, but even so prediction for this class seems problematical. As discussed above, this may be due to complexities in the effects of structure on p°_{L} with nitro-containing compounds, or accuracy problems with the experimental data.

Figure 10 shows σ_{FIT} at various T by major compound class. For some classes, e.g., amides and peroxides, the mean error is least for T values in the center of the fitted range, and larger at both T<300 K and T>360 K. This type of parabolic behavior in the error is typical of least-squares fitting carried out over a specific data range for the independent variable. The relatively larger errors at lower T for all classes are likely exacerbated due to the increase in experimental difficulty at low p°_{L}. Evidence of this difficulty at low p°_{L} is shown in Fig. 11 using data for nitroethanol. Fig. 12 plots σ_{FIT} vs. $\log_{10}(p^{\circ}_{\mathrm{L},i}(T_{j,i}))_{\mathrm{E}}$, again showing the general tendency in the error to increase with decreasing $\log_{10}(p^{\circ}_{\mathrm{L},i}(T_{j,i}))_{\mathrm{E}}$. The increase in σ_{FIT} with decreasing p°_{L} is most likely a combination of the relatively small number of data points at low vapor pressure, the increase in experimental error with decreasing volatility, and the parabolic error profile for a least-squares type of approach.

3.4 $\Delta H_{\mathrm{vap},i}$ prediction using SIMPOL.1 with final coefficients

Values of $\Delta H_{\mathrm{vap},i}$ may be predicted using Eq. (10) and the final B coefficients in Table 5. Figure 13 shows

predicted values of $\Delta H_{\mathrm{vap},i}$ at T=333.15 K vs. experimentally based values derived by consideration of the experimental $p^{\mathrm{o}}_{\mathrm{L},i}=f_i(T)$ functions and Eq. (9). Table 8 summarizes the quality of the predictions at T=333.15 K based on the following un-normalized (σ) and normalized (i.e., relative, ρ) error estimates, with each in absolute value and signed form:

$$\sigma_{\Delta H} = \frac{1}{N}\sum_i \left|(\Delta H_{\mathrm{vap},i})_{\mathrm{P}} - (\Delta H_{\mathrm{vap},i})_{\mathrm{E}}\right| \quad (15)$$

$$\sigma_{\Delta H\_\mathrm{SGN}} = \frac{1}{N}\sum_i \left((\Delta H_{\mathrm{vap},i})_{\mathrm{P}} - (\Delta H_{\mathrm{vap},i})_{\mathrm{E}}\right) \quad (16)$$

$$\rho_{\Delta H} = \frac{1}{N}\sum_i \left|\frac{(\Delta H_{\mathrm{vap},i})_{\mathrm{P}} - (\Delta H_{\mathrm{vap},i})_{\mathrm{E}}}{(\Delta H_{\mathrm{vap},i})_{\mathrm{E}}}\right| \quad (17)$$

$$\rho_{\Delta H\_\mathrm{SGN}} = \frac{1}{N}\sum_i \left(\frac{(\Delta H_{\mathrm{vap},i})_{\mathrm{P}} - (\Delta H_{\mathrm{vap},i})_{\mathrm{E}}}{(\Delta H_{\mathrm{vap},i})_{\mathrm{E}}}\right) \quad (18)$$

For all compounds, $\sigma_{\Delta H}$=8.9 kJ mol^{-1}, $\sigma_{\Delta H\_\mathrm{SGN}}$=2.7 kJ mol^{-1}, $\rho_{\Delta H}$=0.16 (i.e., 16%), and $\rho_{\Delta H\_\mathrm{SGN}}$=0.080 (i.e., 8%). Overall, the fit is reasonably good, especially considering that the fitted quantity was not $\Delta H_{\mathrm{vap},i}$ but rather the underlying $p^{\mathrm{o}}_{\mathrm{L},i}(T)$ functionalities.

3.5 Temperature dependence of $\Delta H_{\mathrm{vap},i}$ using SIMPOL.1 with final coefficients

As noted above, theoretical considerations indicate that $d\Delta H_{\mathrm{vap},i}/dT<0$ for any real compound below its critical temperature $T_{c,i}$. Examination of values returned by Eq. (10) with Eq. (11) indicate that while imperfect, the results are encouraging in this regard, with 408 of the 456 compounds considered returning $d\Delta H_{\mathrm{vap},i}/dT<0$ for T=335.15 K. The results by compound class and sub-class are given in Table 9.

At any given $T<T_{c,i}$, though we know that $d\Delta H_{\mathrm{vap},i}(T)/dT<0$ (see above), this does not require for any particular group k that $d\Delta h_{\mathrm{vap},k}(T)/dT<0$, only that the $\upsilon_{k,i}-$ weighted sum is negative. However, since all $\upsilon_{k,i}\geq 0$, by Eq. (11), at least some fraction of the structurally important groups must give $d\Delta h_{\mathrm{vap},k}(T)/dT<0$. Table 6 gives the sign of the $d\Delta h_{\mathrm{vap},k}(T)/dT$ values at 293.15 K for the SIMPOL.1 groups based on Eq. (11) and the B values in Table 5. Importantly, for the carbon group (k=1), $d\Delta h_{\mathrm{vap},k}(T)/dT<0$. This result is important in causing $d\Delta H_{\mathrm{vap},i}(T)/dT<0$ to be predicted for many of the compounds in Tables 1 and 3.

For the method of Capouet and Müller (2006), taking the derivative of Eq. (3) with respect to $(1/T)$ and consideration of Eq. (9) yields

$$\Delta H_{\mathrm{vap},i}(T)=\Delta H_{\mathrm{vap,hc}-i}(T)-2.303R\sum_k \upsilon_{k,i}\frac{d\,\tau_k(T)}{d(1/T)} \quad (19)$$

and

$$\frac{d\Delta H_{\mathrm{vap},i}(T)}{dT}=\frac{d\Delta H_{\mathrm{vap,hc}-i}(T)}{dT} -2.303R\sum_k \upsilon_{k,i}\frac{d}{dT}\frac{d\,\tau_k(T)}{d(1/T)} \quad (20)$$

The analogous expressions for the SIMPOL.1 representation are Eqs. (10) and (11), respectively.

The functionality selected for the $b_k(T)$ as fitted by Capouet and Müller (2006) is $\tau_k(T)=\alpha_k+\beta_k T$, giving $d\,\tau_k(T)/d(1/T)=-\beta_k T^2$ and $(d/dT)d\,\tau_k(T)/d(1/T)=-2\beta_k T$. In the fitting results reported by Capouet and Müller (2006), all $\beta_k>0$. Thus in that fitting, the role of forcing $d\Delta H_{\mathrm{vap},i}(T)/dT<0$ must then be borne entirely by $d\Delta H_{\mathrm{vap,hc}-i}(T)/dT$. This is not possible for any real compound i. The latter derivative is only capable of bringing $\Delta H_{\mathrm{vap,hc}-i}(T)$ to zero, and for the groups considered by Capouet and Müller (2006), $\Delta H_{\mathrm{vap},i}(T)>\Delta H_{\mathrm{vap},hc-i}(T)$. Caution should therefore accompany use of the temperature dependencies given for the τ_k in Capouet and Müller (2006).

Overall, regardless of the $p^{\mathrm{o}}_{\mathrm{L}}(T)$ prediction method used when modeling the atmospheric behavior of a compound over a particular T interval, when it is correctly predicted over the entire interval that $d\Delta H_{\mathrm{vap},i}/dT<0$, then the T dependence given by Eq. (10) may be used. However, when $d\Delta H_{\mathrm{vap},i}/dT>0$ over some portion of the T interval of interest, $\Delta H_{\mathrm{vap},i}$ should be evaluated at the central T and then assumed to remain constant over the entire interval.

4 Conclusions

A simple group contribution method has been developed that allows prediction of $p^{\mathrm{o}}_{\mathrm{L},i}$ and $\Delta H_{\mathrm{vap},i}$ values based on straightforward molecular structure considerations. Extensive error analyses for both parameters provide a detailed understanding of the reliability of the estimates by compound class and sub-class.

One of the implications of this work is related to the information in Figs. 10, 11, and 12. There is an obvious increase in error of the fit at low vapor pressures and temperatures. The reasons for this are related to the difficulty of making accurate measurements of $p^{\mathrm{o}}_{\mathrm{L},i}$ for low temperatures and pressures. Improvement in vapor pressure estimation techniques, especially for compounds with $p^{\mathrm{o}}_{\mathrm{L},i}<10^{-10}$ atm will require additional empirical data.

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