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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^o_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 $\log_{10} p^o_{L,i}(T) = \sum_k \nu_{k,i} b_k(T)$ where $\nu_{k,i}$ is the number of groups of type k, and $b_k(T)$ is the contribution to $\log_{10} p^o_{L,i}(T)$ 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 $p^o_{L,i}=f_i(T)$ are available. The range of vapor pressure considered spans fourteen orders of magnitude. The ability of the initially fitted B coefficients to predict p^o_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 $\log_{10} p^o_{L,i}(T)$. 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, $\sigma_{FIT}=0.34$: on average, $p^o_{L,i}(T)$ values are predicted to within a factor of 2. Because $d(\log_{10} p^o_{L,i}(T))d(1/T)$ is related to the enthalpy of vaporization $\Delta H_{vap,i}$, the fitted B provide predictions of $\Delta H_{vap,i}$ based on structure.

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