



# Estimation of the normal boiling point of organic compounds via a new group contribution method



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## ABSTRACT

An improved second order group contribution method is developed to determine the normal boiling point of organic compounds. This method is based on the Joback's first order functional groups with some changes and some newly added functional groups developed from experimental data. Each functional group has a group contribution value, and the contribution values have been optimized using 2036 experimental data of organic components ranging from  $N_C = 1-36$  and  $M_W = 26-555$  ( $\text{g}\cdot\text{mol}^{-1}$ ), including heavy and complex polycyclic aromatic compounds. In this method, it is tried to distinguish most of the structural isomers and stereoisomers by second order functional groups to predict their different normal boiling points. First and second order functional groups of the hydrocarbons and hydrocarbon derivatives containing carbon, hydrogen, oxygen, nitrogen, sulfur, fluorine, chlorine, bromine and iodine atoms, are included in this study. The *fminsearch* mathematical approach from MATLAB software is used in this study to select an optimal collection of functional groups (122 functional groups) and subsequently to develop the model. The results of the new method are compared to several well-known methods. The average absolute deviation of normal boiling point predictions for 2036 organic compounds is found to be 4.35194 K; while the percentage of the average absolute relative deviation is just 1.01075%.

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## 1. Introduction

To carry out design calculations, every engineer needs to know thermo-physical properties such as normal boiling point, freezing point, heats of formation, densities and so on. Many of these properties have been measured and tabulated for pure substances, but thermo-physical properties under extreme conditions are not known usually, because the experiments in this regime are often too difficult and expensive. When the physical properties are not accessible, the estimation methods have to be employed. Although, these methods are not very adequate, sometimes there are no other choices.

The traditional approach is to develop mathematical models to predict the properties. Examples of these models include the large number of activity coefficient models like the UNIFAC model [1] or the equations of state which help us to predict the vapor–liquid equilibrium behavior. As we know, these models do not always work, and typically require some experimental data as the input. To

make models more predictive, group contribution methods have been developed [2]. A group contribution method is used to predict the properties of pure components and mixtures by using group or atom properties. Instead of knowing the properties of hundreds of compounds, only the data for a few dozens of groups have to be known. The vast majority of organic components, for example, are built of carbon, hydrogen, oxygen, nitrogen, halogens, and maybe sulfur or phosphorus, together with a single, a double, and a triple bond, there are only few atom types and three bond types to build thousands of components. The next slightly more complex building blocks of components are functional groups which are themselves built of few atoms and bonds. All organic molecules are formed by attaching other atoms or groups of atoms to the carbon backbone of a hydrocarbon. The physical and chemical properties of these derivative molecules are determined by the specific arrangement of atoms called functional groups [3,4].

The physical properties of compounds are described by a large group of structure related characteristics, such as normal boiling point and critical parameters. Most of these properties have been targeted by different correlations and approaches [5–8]. The boiling point is a fundamental thermo-physical property describing

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the temperature of transition between the saturated vapor and liquid phases. It is clear that if specify the system pressure, the temperature at which pure species a boils is fixed. The normal boiling point of a substance, the temperature at which a pure species boils at a pressure of 1 atm, is well defined. The presence of an essentially nonvolatile solute in a liquid phase of mostly solvent, which the system is at a pressure of 1 atm. It was observed that it always requires a greater temperature to boil in mixture than in pure species. This phenomenon is termed boiling-point elevation. Pure component normal boiling point (NBP) of liquid compounds is of great importance for many applications in the design and simulation of various chemical and biochemical processes as well as for environmental and safety problems [9,10]. In some cases, especially for heavy hydrocarbons in the thermal cracking may occur at high temperatures, so the boiling points at lower pressures are specified. Boiling points of heavy hydrocarbons are usually measured at 1, 10, or 50 mm Hg. The normal boiling point, when available, is one of the most important characterization parameters for hydrocarbons and is frequently used in property estimation methods [9].

It is not always possible to find experimental values for the NBP since measurement is expensive and time consuming or sometimes even difficult or impossible, therefore accurate predictive methods can replace the measurements. The estimated properties are not as precise as the well-made measurements but for many purposes the quality of these estimated properties is sufficient. Predictive methods can also be used to check the results of the experimental work. Almost other thermo-physical properties are predictable from the normal boiling point [11–15], so the precise forecast of boiling point could be quite important. According to the well-known rule of Guldberg [16], the NBP of a liquid can be roughly estimated as the two-thirds of the critical temperature on the absolute scale. The rule is not obeyed by liquids of low boiling point, and even for liquids boiling in the range 293–523 K [17]. So other more accurate predictive methods have been proposed by researchers. Group contribution methods include a very important part of these predictive methods which are briefly described in the next section.

## 2. Group contribution methods for the prediction of normal boiling point

The following general considerations have been proposed to evaluate the prediction policy of the thermo-physical properties [18]:

- i. Generalized methods based on group contributions or corresponding states theories are usually used when no experimental data are available.
- ii. If the substance of interest is listed in the input data file of any methods, that method usually gives better results for that particular substance.

The generalized methods based on the group contributions are usually divided into four different categories listed as follows:

### 2.1. Additive group contribution method

The simplest form of a group contribution method is to determine the component property by summing up the group contributions. In this simple form, it is assumed that the property is linearly dependent on the number of groups. It is also assumed that other groups in the molecule do not alter a groups contribution to the physical property. This simple approach is employed in the Joback and Reid method [19] for normal boiling point and it works

well in a limited range of components and property ranges but may lead to quite large errors outside of the applicable ranges. Joback developed the Lydersen's group contribution scheme [20], added several new functional groups, and calculated some new contribution values to improve the original method. His relation for NBP is given by the following equation:

$$T_b = 198.2 + \sum_k N_k(tbk) \quad (1)$$

where  $T_b$  is normal boiling point, K;  $N_k$  is the number of groups of type  $k$  in molecule, with contribution of  $tbk$ . Joback assumed a constant contribution of the added groups in homologous series like the  $n$ -alkanes, which does not describe the real behavior of the normal boiling points correctly [21]. Instead of the constant contribution a decrease of the contribution with increasing number of groups may give more accurate results. The Joback method usually gives acceptable estimation for mid-sized components, but leads to high deviations for large and small molecules.

### 2.2. Additive group contributions and correlations

In this group of methods the pure additive group contributions are correlated to give the desired property. This following thermodynamic relation may be used.

$$dH = TdS + VdP \quad (2)$$

It is known that during any phase change, temperature and pressure of the system remain constant, so:

$$T_b = \frac{\Delta H_{\text{vap}}(T_b)}{\Delta S_{\text{vap}}(T_b)} \quad (3)$$

several simple relations are available for the estimation of enthalpies of vaporization at the NBP of the liquid. Trouton's rule (Eq. (4)), for example, is only suitable for non-polar liquids, but the Giacalone equation (Eq. (5)) is fairly reliable for both polar and non-polar liquids:

$$\Delta H_{\text{vap}}(T_b) = 88 T_b \quad (4)$$

$$\Delta H_{\text{vap}}(T_b) = \left( \frac{RT_c T_b}{T_c - T_b} \right) \ln P_c \quad (5)$$

As the total interaction between the molecules in the liquid phase is much larger in comparison to the vapor phase, the enthalpy of vaporization can be approximated by the total intermolecular interaction in the liquid phase.

For example in a  $n$ -alkane homologous series, a given member differs from the preceding or succeeding member by the constant difference of  $-\text{CH}_2-$  group. Hence, the volume of the molecule increases linearly with the number of  $-\text{CH}_2-$  groups, but molecules are occasionally tend to tangle to a more or less spherical form, and the outer surface may increases non-linearly. It is assumed that the molecular interaction in the organic liquids should also be proportional to the molecular surface. Fig. 1 clearly shows that the  $\Delta H_{\text{vap}}$  (Btu/lbmol) at the NBP for the  $n$ -alkanes is a function of the molecular weight and can be fitted with a single correlation equation (Eq. (6)) containing molecular weight.

$$\Delta H_{\text{vap}}(T_b) = 3048 \left( M_w^{0.4106} \right) - 6263 \quad (6)$$

Where  $M_w$  is the molecular weight and  $\Delta H_{\text{vap}}(T_b)$  is the enthalpy of vaporization at the NBP. As shown in Fig. 1, molecular weight can be used in properties estimation methods for additional property,

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