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# Vapor pressures and vaporization enthalpies of 5-nonanone, linalool and 6-methyl-5-hepten-2-one. Data evaluation

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ABSTRACT

Vapor pressures and vaporization enthalpies for 5-nonanone, linalool and 6-methyl-5-hepten-2-one seem to be in disarray. Temperature dependences of vapor pressures for these pure compounds were measured by using the static and the transpiration techniques. Molar standard enthalpies of vaporization at the reference temperature were derived. Available literature data on vapor pressures and vaporization enthalpies were collected and analyzed. The consistent data set for each compound was evaluated. Reliable thermodynamic parameters of vaporization were derived and used to test some commonly used predicting procedures.

## 1. Introduction

This work has been inspired by a paper published in this journal recently [1]. This paper presented a descriptor based group contribution model for the prediction of the vaporization enthalpies of organic compounds. The database used in this work consisted of 4320 experimental data points for 2811 compounds. The authors used single experimental values available for 2049 compounds. For the remaining 762 compounds, the arithmetic average was used where multiple values were available. The authors explicitly noted that no attempt was made to choose between the independently determined values, which for the most part differed by less than 9 kJ mol$^{-1}$. The exceptions to this were made for 30 compounds presented in their Table 1, where experimental vaporization enthalpies have shown the spread of values more than 9 kJ mol$^{-1}$. To our surprise in this table we have revealed 13 compounds, which have been carefully evaluated in our lab over the last decade. Under evaluation we understand additional experiments, uniform treatment of the available literature data, consistency tests and final recommendation of the evaluated data sets for parent group of compounds. The presented work is intended as the assistance to the community dealing with structure–property relationships, similar to the one hereby reported [1].

In order to avoid an any misunderstandings, that the aforementioned 13 compounds still need revision of the vapor pressure data we provide a list with these compounds and references as follows: *cis*-1,2-diphenylethylene [2], 1-methylimidazole [3], pyrimidine [4], 1,2-propanediol [5], triethylenetetramine and ethylenediamine [6], formamide [7], *N*-(2-hydroxyethyl) ethylenediamine [8], butyl formate [9], 4-chloroaniline [10], propylene carbonate [11], diethyl oxalate [12], and benzyl alcohol [13]. In any case, any indication of unreliable data suggested by Ref. [1] is valuable advice and identifies questionable compounds that should be remeasured.

In the current study we have been guided by the paper by Gharagheizi et al. [1] and have measured vaporization enthalpies of 5-nonanone and (±)-linalool claimed as unreliable. In addition to that we have studied 6-methyl-5-hepten-2-one whose vaporization enthalpy was available only at high temperatures [14,15].

The aliphatic ketone 5-nonanone is used as industrial solvent and also used as platform chemical for production of liquid hydrocarbon fuels (diesel and gasoline) [16]. The aliphatic alcohol (±)-linalool has wide application as perfume, pesticide, and insecticide component [17]. Just recently, the allergic reaction caused by oxidation of linalool to 6-methyl-5-hepten-2-one has been observed [18]. Moreover, the 6-methyl-5-hepten-2-one is also used in household and hygiene products like cleaning agents and air fresheners [19]. Thus, this compound is involved in oxidation reactions resulting in products responsible for possible adverse health effects in the eyes and airways [19].

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**List of symbols**

| | |
|---|---|
| $p_s$ | Saturated vapor pressure, Pa |
| $p^\circ$ | Standard pressure = $10^5$ Pa |
| $\theta$ | Arbitrary chosen reference temperature for treatment, K |
| $\Delta_l^g G_m^\circ(\theta)$ | Standard Gibbs energy of vaporization at reference temperature, J $\text{mol}^{-1}$ |
| $\Delta_l^g H_m^\circ(\theta)$ | Standard enthalpy of vaporization at reference temperature, J $\text{mol}^{-1}$ |
| $\Delta_l^g C_{p,m}^\circ(\theta)$ | Standard heat capacity difference at reference temperature, J $\text{K}^{-1}$ $\text{mol}^{-1}$ |

In this work, we measured the temperature dependence of vapor pressure for 5-nonanone, linalool and 6-methyl-5-hepten-2-one by using static and transpiration techniques and molar standard enthalpies of vaporization were derived. From our experience, reliable evaluation of the experimental data can be performed, provided that the vapor pressures are independently measured by using at least two different techniques on highly pure sample. Consistency of results, which were obtained in the same lab at different temperature ranges, can be good evidence of the reliability of the data, and can be used as a basis of analysis of the available literature data. Joint treatment of the consistent calculated and literature sets of data for each compound under study results in evaluated data sets, and can be recommended for use in further thermochemical calculations. The data is useful for assessing the environmental fate of compounds under study, as well as for further refinement of predicting schemes.

## 2. Experimental

### 2.1. Materials

The samples used for experiments were of commercial origin. The origin of samples and their initial purity are given in Table 1. Prior to the experiments, the samples were purified by repeated vacuum fractional distillation under reduced pressure. The final degree of sample purity was determined by using a gas chromatograph (GC) with a flame ionization detector. A capillary column, HP-5, was used with a column length of 30 m, an inner diameter of 0.32 mm, and a film thickness of 0.25 mm. The standard temperature program of the GC was $T$ = 333.15 K for 180 s followed by a heating rate of 0.167 K $\text{s}^{-1}$ to $T$ = 523.15 K. No impurities (greater than mass fraction 0.001) could be detected in the samples used for the vapor pressure measurements (see Table 1). Samples were additionally purified during an *in situ* preconditioning in the experimental setups.

### 2.2. Vapor pressure measurements. Static method

The static method is one of the best established methods traditionally used for vapor pressure measurements in a broad temperature range [20]. In this work, we used a self-made experimental setup. The cylindrical cell (made of 316Ti stainless steel with the internal volume of 20 $\text{cm}^3$) was tightly connected to a tubing system with a VCR8 connector. The measuring cell was embedded into an aluminum heating block, where the temperature was kept constant within ±0.02 K. The uncertainty of absolute temperature determination was ±0.05 K over the working temperature interval of the system of (253–463) K.

The temperature of tubing connections between the measuring cell and pressure gauges was kept higher than those of the sample cell (by 30–50 K for liquid samples) in order to avoid condensation of sample vapors in the tubing system. For this purpose, we used an air circulation thermostat with the temperature stability of ±0.2 K. The sample cell was connected to a high temperature capacitance manometers (MKS Instruments, Inc.) with the working range of (0.1–$10^5$) Pa with the uncertainty of $\pm 5 \times 10^{-3}\ p$ as stated by the manufacturer.

The detailed description of the experimental apparatus, procedure and uncertainty analysis is given in the Supporting information (see Fig. S1 and Table S1). The validation of the experimental setup and measuring technique was performed using experiments with benzoic acid, naphthalene, ferrocene and benzophenone as reference compounds (see Table S2 and Figs. S1–S6 in electronic Supporting materials). Uncertainties of experimental vapor pressures were calculated according to the following equations:

$$u\left(\frac{p}{\text{Pa}}\right) = 0.0005 + 0.005\left(\frac{p}{\text{Pa}}\right) \quad \text{for } p_s < 12\text{Pa} \qquad (1)$$

$$u\left(\frac{p}{\text{Pa}}\right) = 0.05 + 0.005\left(\frac{p}{\text{Pa}}\right) \quad \text{for } p_s > 12\text{Pa} \qquad (2)$$

#### 2.2.1. Experimental procedure: check for leaks

A possible leak in the apparatus could disturb the vapor pressure measurement. Prior to any experiment with a compound, the empty measuring cell was connected to the system, which was evacuated to a pressure of $10^{-5}$ Pa with an Agilent HS-2 diffusion pump combined in tandem with an Agilent DS 202 rotary vane pump. The static apparatus was then disconnected from the vacuum pump. If any pressure increase due to residual desorption from the tubing was detected, the heating and evacuation of the metal tubing was continued at a higher temperature and it was baked out at 473 K until no pressure increase was observed. Thus, the preliminary check for leaks was completed.

#### 2.2.2. Experimental procedure: sample degasing

The purification procedures, as well as vacuum treatment are very helpful, but they do not allow removing the dissolved gases completely. As a rule, after loading the sample into the cell, it still contains small amounts of dissolved gases, moisture or solvents, which have to be withdrawn from the sample before the start of data acquisition. For this purpose the first series of vapor pressure measurements on the sample was considered as a conditioning procedure leading to the *in situ* degassing and purification of the sample inside of the measuring cell. If three to five consecutive runs at a selected temperature resulted in a constancy of the

**Table 1**
Provenance and purity of the materials.

| Material | CASRN | Origin | GC purity (mass fraction)[a] |
|---|---|---|---|
| 5-Nonanone | 502-56-7 | Sigma–Aldrich, 98% | 0.999 |
| (±)-Linalool | 78-70-6 | Sigma–Aldrich, 97% | 0.999 |
| 6-Methyl-5-hepten-2-one | 110-93-0 | Sigma–Aldrich, 99% | 0.999 |

[a] Purity after fractional distillation under reduced pressure.