



# Critical point measurement of some polycyclic aromatic hydrocarbons



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## ABSTRACT

The critical temperatures and the critical pressures of five polycyclic aromatic compounds, namely, acenaphthene, fluorene, anthracene, phenanthrene, and pyrene have been measured. All the compounds studied decompose at near-critical temperatures. A pulse-heating technique applicable to measuring the critical properties of thermally unstable compounds has been used. The times from the beginning of a heating pulse to the moment of reaching the critical temperature were from (0.06 to 0.85) ms. The short residence times provide little degradation of the substances in the course of the experiments. The experimental critical parameters of the polycyclic aromatic compounds have been compared with those estimated by five predictive methods. The acentric factors of polycyclic aromatic compounds studied have been calculated.

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAH's) are hydrocarbons with two or more benzene rings arranged in various configurations. PAH's are contained in petroleum and coal liquids and are of interest for these liquids processing industry. Besides, PAH's are formed during the incomplete combustion of various fuels by pyrosynthesis from low hydrocarbons and by pyrolysis from higher hydrocarbons. PAH's are widely distributed in the atmosphere and are environmental pollutants identified as suspected carcinogens [1–3]. Vapour–liquid critical properties are important constants of pure compounds. They are used in many correlations for thermophysical properties of gases and liquids [4].

This paper reports the experimental critical temperatures and pressures of five PAH's. These compounds along with their Chemical Abstracts Service Registry Numbers are as follows: acenaphthene (83-32-9), fluorene (86-73-7), anthracene (120-12-7), phenanthrene (85-01-8), and pyrene (129-00-0). To our knowledge, the critical properties of these compounds have never been measured directly. Cheng [5] measured the critical temperatures  $T_c$  of (benzene + phenanthrene) mixtures up to 29 mol% of phenanthrene and by extrapolating these data estimated  $T_c$  of pure phenanthrene ( $T = 869.3$  K). He also noticed the instability of (benzene + phenanthrene) mixtures with more than 15 mol% of phenanthrene at their critical temperatures. The temperature of meniscus disappearance increased with time for such mixtures. Cheng could measure the critical temperatures of

(benzene + anthracene) mixtures only up to 10 mol% of anthracene. He estimated the critical temperature of anthracene (873 K) by assuming that its  $T_c/T_b$ , where  $T_b$  is the normal boiling temperature, is equal to that of phenanthrene. Cheng found out that phenanthrene and anthracene were unstable at their critical points. One may expect that the other PAH's studied in this work are unstable at their critical temperatures too. To measure the critical temperatures and pressures of these PAH's we used the pulse-heating method applicable to thermally unstable compounds.

## 2. Experimental

### 2.1. Materials

The samples of PAH's were purchased from Alfa Aesar and used without any further purification. The Chemical Abstracts Service Registry Numbers (CASRN's) and purities of the samples according to the supplier data are listed in [table 1](#).

### 2.2. Method

The critical temperatures and the critical pressures of PAH's have been measured by the pulse-heating method that has been used by our team for many years [6–10]. The pulse-heating method is based on the phenomenon of liquid superheat and consists in measuring the pressure dependence of the temperature of the attainable superheat (the line of the attainable superheat) with the help of a platinum wire probe heated by electric current pulses. The line of the attainable superheat ends at the critical point so with increasing pressure the temperature of the attainable

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superheat tends to the critical temperature. A probe  $2 \times 10^{-3}$  in diameter and (1 to 3) cm in length which was immersed into a liquid under study and served simultaneously as a heater and a resistance thermometer, was heated by electric current pulses in such a way that by the end of a pulse the probe temperature reached the temperature of the attainable superheat. The duration of heating pulses  $t^*$  was from (0.06 to 0.85) ms in various experiments. Short heating times provided a small decomposition of unstable compounds in the course of measuring the critical properties.

The values of the critical temperature and the critical pressure which are measured in the pulse-heating experiments,  $T_c^m$  and  $p_c^m$ , are always lesser than the true critical temperature  $T_c$  and pressure  $p_c$ . The true critical parameters are calculated for stable compounds by the following equations:

$$p_c = p_c^m / \pi_0, T_c = T_c^m / \tau_0, \quad (1)$$

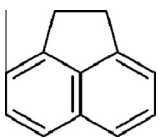
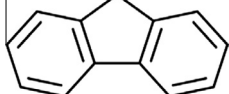
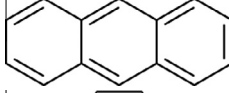
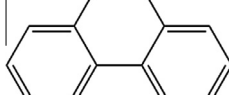
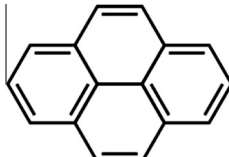
where  $1/\pi_0$  and  $1/\tau_0$  are correction factors. A new method of calculation of the correction factors have been developed lately [10,11]. The method was used in this work. To calculate the correction factors, some properties of a compound under study near the critical point are required. They are estimated by the principle of corresponding states using the similarity parameter  $A$  suggested by Filippov [12]:

$$A = 100 \frac{p_{vp}(T/T_c = 0.625)}{p_c}. \quad (2)$$

Here  $p_{vp}$  is the vapour pressure at a reduced temperature equal to 0.625.

The critical properties and the Filippov parameters of PAH's were calculated by an iteration method. The measured values of the critical properties,  $p_c^m$  and  $T_c^m$ , were used as the critical constants for the first iteration. The vapour pressure at a reduced temperature  $T/T_c = 0.625$  was estimated using the Antoine equation with parameters given in the NIST Chemistry WebBook [13]. Then

**TABLE 1**  
Structural formulae, Chemical Abstracts Service Registry Numbers (CASRN's), and mole-fraction  $x$  purities of compounds (supplier's data, GC) used in critical point measurement.

Compound	Structural formula	CASRN	$10^2 \cdot x$
Acenaphthene		83-32-9	98.0
Fluorene		86-73-7	98.1
Anthracene		120-12-7	99.5
Phenanthrene		85-01-8	98.0
Pyrene		129-00-0	98.3

the Filippov parameters, the correction factors, and the critical properties were calculated. These values were used in the second iteration. Two iterations were enough because the correction factors slightly depend on the Filippov parameter. The ideal gas heat capacity that was used in the calculation of the correction factors was estimated by the atomic contribution method of Rihani and Doraiswamy, as is presented by Reid *et al.* [14]. For a thermally unstable compound, the apparent critical temperature and pressure measured in the pulse-heating experiments may depend on the duration of the heating pulse due to the decomposition of the compound. The durations of the heating pulses were (0.06, 0.11, 0.22, 0.46, and 0.85) ms in our experiments. The probe lengths were (1, 2, and 3) cm, and three or four samples of each compound were used. As no obvious dependence of the apparent critical parameters on the duration of the heating pulse was found for the investigated PAH's, the measured values of the critical temperature  $T_c^m$  and pressure  $p_c^m$  were determined by averaging over all the heating times, lengths, and samples.

### 2.3. Uncertainties

The uncertainties of the critical properties measured by the pulse-heating method were discussed in detail in our previous papers [9,10,15]. It has been shown that the uncertainties are  $\delta p_c = 0.03p_c$ ,  $\delta T_c = 0.01T_c$  for low-molar-mass compounds and  $\delta p_c = 0.04p_c$ ,  $\delta T_c = 0.015T_c$  for compounds with high acentric factors  $\omega \geq 1$  or with strong hydrogen bonding, where  $T_c$  is the absolute temperature. PAH's studied have no hydrogen bonds and, according to our estimation, the acentric factors of these compounds fall in the range (0.358 to 0.402) (see table 3) so that they may be considered as "usual" low-molar-mass compounds. The uncertainties are from  $\pm 0.09$  to  $\pm 0.11$  MPa for the critical pressure and from  $\pm 8$  to  $\pm 10$  K for the critical temperature. Here the uncertainties are the combined expanded uncertainty at the 95% level of confidence.

The samples of PAH's used in this study, except anthracene, have about 2 mol% of impurities (see table 1). Naturally, there arises the question about the effect of the impurities on the critical properties and uncertainties. This effect is difficult to estimate. For such estimation, one should know the chemical composition of the impurities and the critical locus curve as a function of the composition. Unfortunately, the composition of the impurities is unknown. One may suggest that the samples of PAH's contain isomers of the main compound and compounds which are close to the main one on the structure of the molecules. Let us use a (benzene + toluene) mixture as a model for (PAH + impurity) systems. The critical curve of a (benzene + toluene) mixture was measured by Kay and Hissong [16]. With the use of these data the differences between the critical temperatures and pressures of pure toluene [17] and the mixture that contains 0.2 mol% of benzene are about 0.3 K and 0.02 MPa. These values are considerably lower than the uncertainties given above. The estimation made is very rough but we believe that the presence of impurities in the samples of PAH did not influence appreciably the critical properties obtained.

### 3. Results and discussion

The critical temperatures and pressures of PAH's measured in this study are given in tables 2 and 3. The critical properties of PAH's were also estimated using five methods. In general, there are several approaches to the estimation of the critical parameters of PAH's. In particular, the critical constants of these compounds can be calculated by group contribution methods both suitable for a wide variety of pure organic compounds (see, for instance, [4,14,18–25] and many others) and developed specially for heavy

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