

# EQUATION OF STATE OF HYDROCARBONS FOR THE LIQUID PHASE

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## Abstract

*It is necessary to construct equations of state that qualitatively and quantitatively accurately reflect the behavior of the thermodynamic surface in the considered range of parameters, in order to compile tables of the thermodynamic properties of liquids. A sufficient amount of high-precision experimental data on the P-V-T dependence is necessary to constructing such equations. Most of the equations are not suitable for extrapolation, they are valid in limited areas of state parameters. An equation of state with three coefficients is proposed to describe the P-ρ-T dependence of liquid hydrocarbons of various molecular structures (benzene, n-octane, isooctane, octene-1).*

**Keywords:** equation, liquid, hydrocarbons, density, thermodynamic

## I. Introduction

First of all, it is necessary to construct equations of state that qualitatively and quantitatively accurately reflect the behavior of the thermodynamic surface in the considered range of parameters, in order to compile tables of the thermodynamic properties of liquids. A sufficient amount of high-precision experimental data on the P-V-T dependence is necessary to constructing such equations. Most of the equations are not suitable for extrapolation, they are valid in limited areas of state parameters.

The equations of state for condensed phases are usually divided into two groups. The first includes equations of  $\rho=f(P, T)$  type, the second -  $P=f(\rho, T)$  type. Since in practice determination of the liquid density ( $\rho$ ) depending on pressure ( $P$ ) and temperature ( $T$ ) is most often required, in our opinion, preference should be given to equations of the first type.

From this point of view, let's consider the two equations of state known from the literature sources, which have a simple structure and are currently used.

## II. Results

Earlier [1], using the expansion of the potential forces of intermolecular repulsion in a series in powers of  $1/r^9$ , a simple equation of state of forces for highly compressed gases was obtained in the form:

$$\rho^4 = A + BP, \quad (1)$$

where  $r$  is the intermolecular distance:  $A, B$  are temperature-dependent coefficients.

The authors of [1] assumed that the possibility of applying equation (1) to the liquid phase can be ensured by introducing a correlation term proportional to  $\rho^7$  into the left side of the equation. However, the application of this equation to liquid benzene, n-octane, isooctane, and 1-octene has shown that this assumption is not justified.

The equation of state for the liquid phase is also known [2]:

$$P = C\rho^2 + D\rho^8, \quad (2)$$

where  $C, D$  are coefficients that are functions of temperature.

Calculations carried out according to equation (2), on the example of benzene, n-octane, isooctane, and octene-1, showed that it is a local equation, which can be considered sufficiently accurate for a limited temperature range. For the range of parameters close to the saturation curve and for higher temperatures, the error of the equation increases, going beyond the limits of the experimental error. The foregoing dictated the need to compile another equation suitable for a wide range of parameters. We can propose a new equation of state with three coefficients, using the precision experimental results on the  $P$ - $V$ - $T$  dependence obtained earlier for benzene [3], n-octane [4], isooctane and 1-octene [5]. This is achieved by introducing an initial approximation that allows an exact and practical equation to be obtained. Equation (1) can be taken as such an approximation. If we introduce a correlation term into the right side of equation (1), which takes into account this interaction of molecules and is proportional to  $P^{0.5}$ , we can obtain a semi-empirical equation of state

$$\rho^4 = E + FP^{0.5} + KP, \quad (3)$$

where  $E, P, K$  are constants depending on  $T$  and determined from experimental data.

$E, P, K$  are calculated for each isotherm by the least squares method and are presented as:

$$E(T) = \sum_{i=0}^L e_i T^i, \quad F(T) = \sum_{i=0}^m f_i T^i, \quad K(T) = \sum_{i=0}^n k_i T^i, \quad (4)$$

The values of standard deviations  $\sigma$  were used as the main criterion for determining the values of  $L, m$ , and  $n$ . The minimum value of standard deviation (approximately 0.05%) was obtained at the value  $L=5, m=6$  and  $n=6$ . The data obtained are internally consistent within the measurement error, which, in particular, can be judged from the values of  $\sigma$ . The maximum error of equation (3) did not exceed the experimental error. The coefficients of the polynomials  $e_i, f_i, k_i$  are given in Table 1 for each hydrocarbon. To confirm the advantages of equation (3) over equation (2), Table 2 compares the calculated density values according to (3) with the experimental ones for the largest deviations of the calculated data from the experimental values. The density values calculated by equation (2), are also given here, the coefficients of which are determined by the formulas:

$$C(T) = \sum_{i=0}^4 c_i T^i, \quad D(T) = \sum_{i=0}^L d_i T^i, \quad (5)$$

The values of the coefficients  $c_i, d_i$  are presented in table 3 for benzene, n-octane, isooctane and octene-1. Experimental data given in table 2 cover the range of state parameters in the temperature range 298–550 K and pressures 0.1–60 MPa. The maximum experimental error did not exceed 0.1% [3–8]. It follows from the results of a quantitative analysis of the equation of state (3) that it describes the experimental density values with an arithmetic mean error of 0.07%.

The maximum deviation is observed at some points at a temperature above 535 K and a pressure of 5 MPa and reaches 0.18% for benzene, 0.16% for n-octane, 0.15% for isooctane, and 0.18% for octene-1. Although equation (2), gives an insignificant error in a certain range of state parameters, the calculation error goes beyond the experimental error at low pressures and elevated temperatures. The maximum error is: 1.08% for benzene, 0.61% for n-octane, 0.33% for isooctane, and 0.2% for octene-1.

**Table 1:** Values of coefficients  $e_i$ ,  $f_i$ ,  $k_i$  in equation (4)

I	$e_i$	$f_i$	$k_i$	$e_i$	$f_i$	$k_i$
	<b>Benzene</b>			<b>Octane</b>		
0	4.5642675	2.8068478	$-6.671474 \cdot 10^{-2}$	-3.672235	-6.273416	0.5573032
1	$-4.438599 \cdot 10^{-2}$	$-4.158414 \cdot 10^{-2}$	$9.381676 \cdot 10^{-4}$	$5.1682781 \cdot 10^{-2}$	$9.9653413 \cdot 10^{-2}$	$-8.979502 \cdot 10^{-3}$
2	$2.204459 \cdot 10^{-4}$	$2.586033 \cdot 10^{-4}$	$-5.706132 \cdot 10^{-6}$	$-2.593095 \cdot 10^{-4}$	$-6.503957 \cdot 10^{-4}$	$5.9415086 \cdot 10^{-5}$
3	$-5.876978 \cdot 10^{-7}$	$-8.653627 \cdot 10^{-7}$	$1.984129 \cdot 10^{-8}$	$6.2711190 \cdot 10^{-7}$	$2.2321880 \cdot 10^{-6}$	$-2.064034 \cdot 10^{-7}$
4	$7.866661 \cdot 10^{-10}$	$1.643922 \cdot 10^{-9}$	$-4.111333 \cdot 10^{-11}$	$-7.461305 \cdot 10^{-10}$	$-4.249299 \cdot 10^{-9}$	$3.9725142 \cdot 10^{-10}$
5	$4.187993 \cdot 10^{-13}$	$-1.678311 \cdot 10^{-12}$	$4.712289 \cdot 10^{-14}$	$3.5040744 \cdot 10^{-13}$	$4.2560733 \cdot 10^{-12}$	$-4.018655 \cdot 10^{-13}$
6	-	$7.187356 \cdot 10^{-16}$	$-2.293186 \cdot 10^{-17}$	-	$-1.752868 \cdot 10^{-15}$	$1.6701624 \cdot 10^{-16}$
	<b>Isooctane</b>			<b>Octane</b>		
0	-2.1946643	-4.57027907	0.35852866	-0.1121524	1.33260615	-0.1129255
1	$3.1459937 \cdot 10^{-2}$	$7.2166291 \cdot 10^{-2}$	$-5.686986 \cdot 10^{-3}$	$6.4960058 \cdot 10^{-3}$	$-1.7526046 \cdot 10^{-2}$	$1.4601022 \cdot 10^{-3}$
2	$-1.531496 \cdot 10^{-4}$	$-4.660612 \cdot 10^{-4}$	$3.6901908 \cdot 10^{-5}$	$-2.974276 \cdot 10^{-5}$	$9.62322381 \cdot 10^{-5}$	$-7.778939 \cdot 10^{-6}$
3	$3.5723606 \cdot 10^{-7}$	$1.5779663 \cdot 10^{-6}$	$-1.253415 \cdot 10^{-7}$	$5.1075569 \cdot 10^{-8}$	$-2.8487845 \cdot 10^{-7}$	$2.2305132 \cdot 10^{-8}$
4	$-4.131405 \cdot 10^{-10}$	$-2.958711 \cdot 10^{-12}$	$2.356017 \cdot 10^{-10}$	$-3.476646 \cdot 10^{-11}$	$4.8312956 \cdot 10^{-10}$	$-3.670581 \cdot 10^{-11}$
5	$1.9034547 \cdot 10^{-13}$	$2.9185297 \cdot 10^{-12}$	$-2.328967 \cdot 10^{-13}$	$4.5888767 \cdot 10^{-15}$	$-4.460354 \cdot 10^{-13}$	$3.3119051 \cdot 10^{-14}$
6	-	$-1.184841 \cdot 10^{-15}$	$9.4734939 \cdot 10^{-17}$	-	$-1.7519963 \cdot 10^{-16}$	$-1.286134 \cdot 10^{-17}$

**Table 2:** Comparison of experimental hydrocarbon density values with those calculated using equations (2) and (3)

T(K)	Pressure, P (MPa)													
	5		9.9		19.7		29.5		39.3		49.1		58.9	
	$\rho$ (kg/m <sup>3</sup> )	$\Delta$ (%)												
<b>Benzene</b>														
505.95	616.9*		642.6		676.2		700.3		719.2		734.5		748.6	
	618.6**	-0.26	642.6	0.00	676.3	-0.01	700.6	-0.03	719.8		735.8	-0.17	749.6	-0.12
	616.9***	0.00	642.5	+0.01	675.7	+0.07	699.4	+0.12	718.9	0.04	733.7	+0.11	747.4	+0.15
<b>Octane</b>														
548.18	507.4		567.1		624.8		657.6		681.4		699.8		716.6	
	511.8	-1.08	565.3	+0.31	621.2	+0.57	655.3	+0.34	680.4	+0.14	700.3	-0.07	717.0	-0.05
	508.4	-0.18	566.3	+0.14	623.8	+0.16	657.3	+0.04	681.0	+0.06	699.2	+0.08	715.9	+0.09
<b>Octane</b>														
534.40	475.7		505.1		539.8		562.8		580.1		594.3		607.1	
	476.7	-0.20	504.2	+0.18	538.8	+0.18	562.1	+0.11	580.0	+0.01	594.6	-0.05	607.0	+0.01
	475.2	-0.10	505.9	-0.15	540.3	-0.09	563.3	-0.08	581.1	-0.14	595.3	-0.17	607.9	-0.12

559.55	438.4		477.8		515.2		542.9		565.9		580.6		593.3	
	439.7	-0.29	477.1	+0.13	518.9	-0.61	545.3	-0.44	565.0	+0.16	580.7	-0.02	594.0	-0.11
	437.7	+0.16	477.1	+0.13	514.3	+0.17	542.1	+0.14	565.0	+0.16	580.0	+0.09	594.2	-0.15
<b>Isooctane</b>														
506.75	492.9		521.1		555.1		577.5		595.4		609.3		621.1	
	493.6	-0.14	519.9	+0.23	553.8	+0.24	576.9	+0.11	594.7	+0.11	609.3	0.00	621.8	-0.11
	492.9	0.00	520.9	+0.03	554.7	+0.06	577.3	+0.03	594.7	+0.12	608.9	+0.05	621.1	0.00
<b>Octene - 1</b>														
538.65	445.5		486.1		529.9		556.2		575.9		592.0		605.3	
	447.0	-0.33	485.8	+0.07	528.8	+0.21	555.9	+0.06	576.0	-0.01	592.1	-0.02	605.7	-0.06
	446.2	-0.15	486.6	-0.09	530.1	-0.04	557.1	-0.16	576.9	-0.17	592.7	-0.11	605.8	-0.07
<b>Octene - 1</b>														
410.45	632.4		641.4		656.2		667.4		677.4		687.7		695.9	
	632.3	+0.01	640.7	+0.11	655.1	+0.16	667.3	+0.01	677.9	-0.06	687.2	+0.06	695.7	+0.03
	632.0	+0.06	641.1	+0.04	655.3	+0.13	667.1	+0.05	677.5	-0.01	686.9	+0.11	695.7	+0.03

538.95	488.9		519.7		555.1		579.6		597.6		612.4		625.9	
	489.9	-0.20	518.8	+0.17	554.9	+0.03	579.2	+0.07	597.7	-0.01	612.8	-0.07	625.7	+0.03
	489.5	-0.13	519.5	+0.03	555.4	-0.05	579.3	+0.04	597.7	-0.02	612.8	-0.07	625.8	+0.02

**Table 3:** The value of the coefficients  $c_i$  and  $d_i$  in equation (5)

<b>Benzene</b>		<b>Octane</b>	
$c_i$	$d_i$	$c_i$	$d_i$
$c_0=-653.7213$	$d_0=4798422$	$c_0=-1987.881$	$d_0=-7010.663$
$c_1=1.052837$	$d_1=1.03874$	$c_1=12.5561$	$d_1=-42.60445$
$c_2=4.256481 * 10^{-3}$	$d_2=1.047337 * 10^{-2}$	$c_2=-3.46486 * 10^{-2}$	$d_2=0.138296$
$c_3=-1.288143 * 10^{-5}$	$d_3=3.224042 * 10^{-5}$	$c_3=4.667809 * 10^{-5}$	$d_3=-1.9160 * 10^{-4}$
$c_4=1.0232120 * 10^{-8}$	$d_4=2.66103 * 10^{-8}$	$c_4=2.416768 * 10^{-8}$	$d_4=1.116106 * 10^{-7}$
<b>Isooctane</b>		<b>Octene - 1</b>	
$c$	$D$	$c$	$d$
$c_0=-727.8638$	$d_0=-4315.087$	$c_0=-323.882$	$d_0=4049.763$
$c_1=1.705612$	$d_1=-25.69849$	$c_1=-1.536156$	$d_1=-33.97943$

### III. Conclusions

Thus, we can recommend the equation of state (3), to calculate the thermodynamic properties of hydrocarbons in the liquid phase in a wide range of parameters.

### References

- [1] Zimmerman S.S., Miniovich V.M. // 1977. V. 51. №1. pp. 208-209.
- [2] Akhundov T.S. Study of the thermophysical properties of aromatic hydrocarbons: Abstract of the thesis, Baku, 1974. p. 57.
- [3] Naziev Ya.M., Gasanov V.G., Naziev J.Ya. / Thermal physics of high temperatures. 1993. V. 31. № 6 pp. 1031-1033.
- [4] Naziev Ya.M., Gasanov V.G., Allahverdiev A.M. and others / AzTU, Baku, 1992. pp. 143-147.
- [5] Naziev Ya.M., Gasanov V.G., Naziev J.Ya. and others. Oil and gas. 1992. № 5-6. pp. 54-56.
- [6] Vagif Hasanov, Ahmad Muslumov, Adila Zeynalova The investigation of the density of n.butanol+n.ok-tan at high parameters/Turkiye, THERMAM, p.136-138, 2019
- [7] Hasanov V.H. Gulshen Aliyeva, Adila Zeynalova, Ahmad Muslumov Thermodynamic and Acoustic Properties of Binary Liquid Mixture / 9th International Conference on Theory and Application of Soft Computing, Computing with Words and Perception, ICSCCW 2017, 24-25 August 2017, Budapest, Hungary
- [8] Hasanov V.H. The Speed of Sound of n-Heptane, n-Octane and their Binary Mixtures at Temperatures  $T=293.15$  to  $523.15$  K and Pressures up to 60 Mpa // High Temperature, vol. 50, No. 1, pp.44-51, 2012, USA.