The Enthalpy and Entnopy of N-Alcanes in the Wide Range of Temperatures and Pressures, Including the Critical Point [1]

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[1] Paper presented at the Thirteenth Symposium on Thermophysical Proporties, June 22-27, 1997, Boulder, Colorado, USA.

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ABSTRACT

On the basis of the author's and the most reliable referense data of isobaric heat capacity data of enthalpy and entropy of n-alcanes n-C_5...n-C_{11} were calculated in the temperature range from the triple point to the temperatures of thermal decomposition (620...670 K) at the pressures up to 60 MPa. As thermodynamic starting point was taken T=0 K. On the basic of the analyses of the obtained data and the most reliable reference data of the initial properties of methane, ethane, propane and n-butane it is shown that the configuration entropy in the critical point of n-alcanes from methane to n-undecane is the constant value (ΔS_c=51.86 ($J \cdot mol^{-1} \cdot K^{-1}$)) in the range of the errors of it's definition. The value of configuration enthalpy in the critical point is a single valued function of the thermodynamic criteria similarity.

KEY WORDS: alcanes; critical point; enthalpy; entropy; equation of state; fundamental crossover equation of state; isobaric heat capacity.

1. INTRODUCTION

During the last 20 years the investigation of isobaric heat-capacity of different hydrocarbons groups and oil fractions in the wide range of state parameters are conducted by the authors with co-workers of the Grozny Petroleum Institute.

Normal alcanes n-C_5...n-C_{11} are investigated in details. Measurements are conducted in the unit of adiabatic flow calorimetry with closed circulation of the substance and calorimentric measurement of the flow rate. The description of the unit is given in the articles [1,2]. There has been investigated the temperature range from 300 K to the beginning of thermal decomposition (620...670 K) at pressures up to 60 MPa including gas and vapour phases, critical and supercritical regions. Obtained experimental data partly published in articles [3...11] compose the necessary base of calculation of the caloric properties of n-alcanes. Thermodynamic diagram of table calculations is shown on the diagram 1.

2. TECHNIQUE OF CALORIC PROPERTIES CALCULATION.

In the temperature range from the triple point to 298.15K isobaric changes of enthalpy and entrophy in the liquid phase are calculated by the local thermal equation of state obtained in [12].

Enthalpy H' and entropy S' data on the saturation line [13] are taken as basic form in the given temperature range. The state of n-alcanes in the form of molecular crystal at the temperature of absolute zero and prssure of saturated vapours is taken as the thermodynamical reference point of enthalpy $H_{oo} = 0$ and entropy $S_{oo} = 0$.

The calculation of enthalphy and entropy at the temperature range above 298.15 K is performed by integration of smoothing experimental data C_p, P, T - authors [3...11]. Enthalpy H' and entropy S' values on saturation line are defined by integration of experimental isobar C_p in liquid phase at precritical pressures in the temperature range from T_o = 298.15 K to the saturation temperature T_s. On supercritical isobars the integration is done from a temperature To to maximum temperature of an experimental T_{max}. At the precritical pressures in gas phase the

integration is conducted from T_{max} to the saturation tamperature T_s. Enthalpy H″ and entropy S″ data on saturation line in gas phase are determined by this method. Special values H and S at the temperature T_{max} and pressures p psc are calculated by generalised Lee and Kesler equation of state [14]. Values H and S obtained at the temperature T_{max} and supercritical pressure $p < p_{sc}$ are taken for the calculation. The reliability of such calculations is tested by the comparison with experimental C_p-data.

Isothermal dimensions H and S for n-C_{10} and n-C_{11} at the temperature T_{max} are calculated by Lee and Kesler equation of state in ideal gas state. Special values H_o and S_o in ideal gas state at the temperature T_o = 298.15 K defined as an auxiliary point indication are determined according relationships:

$$H_0^0 = H_0' + DH_v^{298} + \int_{P_s}^{0} \left(\frac{\partial H}{\partial p}\right)_T \partial p, \qquad (1)$$

$$S_0^0 \approx S_0' + \frac{DH_v^{298}}{T_0} + \ln\left(\frac{p_s^{298}}{p_0}\right), \qquad (2)$$

where ΔH_v^{298} - the enthalpy of vaporisation at the temperature T_o = 298.15 K; H_0', S_0' - enthalpy and entropy on the saturation line of liquid at the temperature T_o (taken according data [13]); p_s^{298} - the vapour pressure at the temperature T_o; p_o = 101325 MPa.

Values ΔH_v^{298} are taken according data [15] and values of vapour pressure are calculated by the equations obtained by Kurumov in [12]. Ideal-gas values of enthalpy and entropy at the temperature T_{max} are defined by integration ideal-gas heat capacity C_p data [16].

Obtained data of enthalpy H′, H″ and entropy S′, S″ on saturation line of liquid and gas permit to calculate the enthalpy of vaporization ΔH_v according thermodynamic identities

$$\Delta H_v = H'' - H', \qquad (3)$$

$$\Delta H_v = T_s(S'' - S'). \qquad (4)$$

Values ΔH_v calculated according (3) and (4) are averaged. Disagreement between them don't exceed 0.5...0.8 $kJ \cdot kg^{-1}$.

3. RESULTS

3.1. Enthalpy and Entropy on the Saturation Line.

Generalisation of data about caloric properties of n-alcanes on the saturation line is conducted in the frames of thermodynamical similarity theory [17]. For enthalpy and entropy of thermodynamic similar subtances the following relationships must be carried out:

$$(S^0 - S')/R = f(\omega,\tau), \quad (5)$$

$$(H^0 - H')/(RT_c) = \varphi(\omega,\tau), \quad (6)$$

where S^0 and H^0 - ideal-gas functions at the suitable temperature; ω - defined criteria of similarity (Pitzer acentric factor is taken in this case [20]).

The implicit form of relationships (5) and (6) is defined by experimental data of authors and literature data [13,18]. In relationships (5) and (6) the point of indication of values S^0 and S', H^0 and H' must be the same. We haven't any problems with entropy because the entropy value at the temperature 0 K is equal to zero for every phase. For generalisation of enthalpy data values H^0 and H' are necessary to count off from one state. Data in reference literature about S^0_{298} and H^0_{298} [19] are calculated from ideal-gas state. This is the reason why it's impossible to use these literature data about H^0_{298} for generalization of H' n-alcanes values from n-C_5 and above, so as data of this work are calculated from the state of molecular crystal. Values H^0_{298} for given alkanes are determined by equation (1). The last component in equation (1) is considered for n-pentane and n-hexane.

Entropy values S^0_{298} are taken in accordance with reference data [19] and for n-alcanes n-C_7... n-C_{11} are also calculated by relationship (2) and generalised.

As the generalisation is conducted in the temperature range from triple point to critical, so initially enthalpy H_c and entropy S_c values are defined at the critical point. These values are obtained by the method of linear diameter of experimental data about H', H'' and S', S''.

The analysis of data shows that comfiguration entropy $\Delta S_c = S_c^0 - S_c$ of n-alcanes at the critical point is constant in limits of error of its definition and dimentionless configuration enthalpy $H_c = (H_c^0 - H_c)/RT_c$ is the function of Pitzer criteria. This is illustrated by the diagram 2. It is necessary to consider that average value of configuration entropy at the critical point is equal to S_c=51.86 $J \cdot mol^{-1} \cdot K^{-1}$ and is quite near the value 6R=49.9 $J \cdot mol^{-1} \cdot K^{-1}$. Obviously this result may have theoretical study. Value H_c is approximated with the equation (7) with SD 0.53%

$$\Delta H_c/(R \cdot T_c) = 2.640 + 1.2842 \cdot \omega - 0.6382 \cdot \omega^2 \qquad (7)$$

Generalized equation for the calculation of configuration enthalpy and entropy is the following:

$$\Delta\tilde{F} = \alpha_1 \cdot (1-\tau) + \alpha_2 \cdot (1-\tau)^2 + \alpha_3 \cdot (1-\tau)^{\beta_0} + \omega \cdot \Big[\alpha_4 \cdot (1-\tau) + \\ + \alpha_5 \cdot (1-\tau)^2 + \alpha_6 \cdot (1-\tau)^{\beta_1} + \alpha_7 \cdot (1-\tau) \cdot \tau_1 \Big], \qquad (8)$$

where $\Delta\tilde{F}$ - dimentionless function, form of which and numerical values are presented in the Table 1.

The character of deviation is shown on Diagrams 3 and 4.

3.2. Enthalpy of Vapourisation

The analysis of calculation methods ΔH_v shows that they are quite reliable in the temperature range from 298.15 K to the normal temperature of boiling. However, considering the universal character of ΔH_v behaviour at $T \rightarrow T_c$ we can suppose that extrapolation in the region of high temperatures will be sufficiently reliable.

Karruto and Kabayashi equation is given for these purposes [20] in the temperature range $0.6 \leq \tau \leq 1$.

$$\frac{\Delta H_v}{RT_c} = 7.08 \cdot (1-\tau)^{0.354} + 10.95 \cdot \omega \cdot (1-\tau)^{0.456} \qquad (9)$$

The base of data ΔH_v, T include data of authors and data presented in [15], also results of n-hexane enthalpy investigation [21] and reference data for C_1... C_4 from [18]. This base of data is done for testing of generalised relationships and constructions and if necessary new ones. We pay attention on the practically absolute absence of ΔH_v experimental data at the temperature below 298.15 K. However, sufficiently reliable estimation of ΔH_v^t at the temperature of triple point may be performed using data of Bondi [22] about enthalpy of sublimation ΔH_s^t and precision data about ΔH_m^t melting of enthalpy given in [13]. Neglecting the value of changes of gas enthalpy at the changes of pressure from saturation to zero (Bondi considers gas as ideal) we get:

$$\Delta H_v^t = \Delta H_s^t - \Delta H_m^t . \qquad (10)$$

Results calculated according formula (10) are used by authors for obtaining special values of enthalpy of vapourisation in the temperature range from triple point to 298.15 K. Special values are defined with step by graphical interpolation in the coordinates H_v - T and H_v - ρ.

The comparison of indicated base of data with calculated according the equaion (9) by values in the range of given temperatures $0.6 \leq \tau \leq 1$ gives the value SD equal to 1.63 %. The following analysis shows that eguation of form (9) may be spread over the low temperature region.

New coefficient of the equation from the given above base of data by approximation of data ΔH_v are the following:

$$\frac{\Delta H_v}{RT_c} = 6.8971 \cdot (1-\tau)^{0.358} + 12.4638 \cdot (1-\tau)^{0.461} . \qquad (11)$$

The value SD in the temperature range from triple point to critical composes 1.20%.

For more accurate calculations there is given the equation of form (8), coefficients of which are presented in the Table 1, but the character of deviation is shown on the Diagram 5.

As we can notice from this drawing deviations of value 2...4% are absorbed only at temperatures exceeding $0.99 \cdot T_c$ that quite corresponds error of determination ΔH_v in this temperature range.

3.3. Enthalpy and entropy in the wide range of state parameters.

There is carried out the analyses of generalised equations of state recommended for the calculation of caloric properties of hydrocarbons. There is established that Lee and Kesler generalised equation of state [14] gives the best results at $\tau \geq 0.5$. The equation is applied not only for calculations of H and S, but also for heat capacity of C_p. Without considering in details the results of C_p calculation we note that the limit of application Lee and Kesler equation of state [14] is determined by the results of comparison with experimental data of authors (outside of which errors of C_p calculation exceed 3...5%).

This area is limited in the low part by saturation line and in high part by isobar $p/p_c = 1.8$ and is extended in the density range $|\Delta\tilde{\rho}| \leq 0.5$.

For predicted calculations of thermodynamical properties in the critical region authors worked out the generalised equation of state based on fundamental crossover equation of state suggested by Sengers and his collaborators [23,24]. Detailed description of generalised equation and procedure of its obtaining is presented in [25]. We consider the application of this equation for enthalpy and entropy calculation. The form of crossover equation of state and all necessary calculated relationships are presented in the Appendix.

The coefficient of compressibility of real substance is defined by relationship:

$$Z = Z^{(0)} + \frac{\omega}{\omega^{(r)}}\left[Z^{(r)} - Z^{(0)}\right], \qquad (12)$$

where Z^0 and $Z^{(r)}$ are coefficients of compressibility of single and standard substances; $\omega^{(r)} = 0.3043$ - the acentric factor of standard substance; ω - the acentric factor of real substance; for simple substance $\omega^{(0)} = 0$.

Functions $Z^{(0)}$ and $Z^{(r)}$ are defined by the following way. We calculate these functions for real substance with defined $\tilde{p}$ and $\tilde{T}$ by crossover equation of state (A.12)...(A.14) and relationship (13) of density of simple $\rho^{(0)}$ and standard $\rho^{(r)}$ substances. We determine coefficients of compressidility by relationships (15) and (16)

$$\tilde{P} = \left[C_\rho\left(1 + B_3 \cdot \Delta\tilde{T}\right) + M\right] \cdot \left(\frac{\partial \Delta\tilde{A}_r}{\partial M}\right)_t - \tilde{A}_0\left(\Delta\tilde{T}\right), \tag{13}$$

$$Z^{(0)} = Z_c^{(0)} \cdot \left[\tilde{p} / \tilde{\rho}\right]^{(0)}, \tag{14}$$

$$Z^{(r)} = Z_c^{(r)} \cdot \left[\tilde{p} / \tilde{\rho}\right]^{(r)}, \tag{15}$$

where $Z_c^{(0)}$ and $Z_c^{(r)}$ - correspondently critical coefficients of compressibility of simple and standard substances.

The density of real substance is calculated by relationship

$$\rho = p/(Z \cdot R \cdot T). \tag{16}$$

Now we can calculate calorific functions. We determine $H^{(0)}$ and $S^{(0)}$ for simple and standard $H^{(r)}$, $S^{(r)}$ substances by crossover equation of state. Then we determine deviations of functions from ideal-gas values:

$$\Delta H^{(0)} = H^{(0)} - H^{0(0)}(T^{(0)}), \quad \Delta S^{(0)} = S^{(0)} - S^{0(0)}(T^{(0)}), \tag{17}$$

$$\Delta H^{(r)} = H^{(r)} - H^{0(r)}(T^{(r)}), \quad \Delta S^{(r)} = S^{(r)} - S^{0(r)}(T^{(r)}), \tag{18}$$

where $T^{(0)} = -T_c^{(0)} / \tilde{T}$, $T_c^{(0)} = 150.663$ K critical temperature of simple substance; $T^{(r)} = -T_c^{(r)} / \tilde{T}$, $T_c^{(r)} = 507.20$ K - critical temperature of standard substance.

Ideal-gas functions are calculated by following relationships:

- simple substance:

$$H^{0(0)} = (5/2)\cdot R\cdot(T - T_0) + H_0^{0(0)}, \tag{19}$$

$$S^{0(0)} = (5/2)\cdot R\cdot \ln(T/T_0) + S_0^{0(0)}, \tag{20}$$

- standard substance:

$$H^{0(r)} = \sum_{i=0}^{3} C_i\cdot(T^{i+1} - T_0^{i+1})/(i+1) + H_0^{0(r)}, \tag{21}$$

$$S^{0(r)} = c_0\cdot \ln(T/T_0) + \sum_{i=0}^{3} C_i\cdot(T^i - T_0^i)/i + S_0^{0(r)}, \tag{22}$$

where values of coefficients C_i are determined by approximation of data [23]: C_0= 11.488; C_1 = 0.4709317; C_2 = - 7.464995·10^{-5}; C_3 = - 9.370616·10^{-8}; $T = T^{(R)}$; T_0 = 298.15 K; $H_0^{0(0)}$ = 6197 J·mol^{-1}; $S_0^{0(0)}$ =154.73 J·mol^{-1}·K^{-1}; $H_0^{0(r)}$ = 65660 J·mol^{-1}; $S_0^{0(r)}$ = 348.95 J·mol^{-1}·K^{-1};

The deviation of enthalpy of real substance from ideal-gas value $\Delta\tilde{H}$ is calculated by the equation

$$\Delta\tilde{H}\cdot\left(\tilde{\rho},\tilde{T}\right) = \Delta\tilde{H}^{(0)}\cdot\left(\tilde{\rho},\tilde{T}\right) + \frac{\omega}{\omega^{(r)}}\left[\Delta\tilde{H}^{(r)}\cdot\left(\tilde{\rho},\tilde{T}\right) - \Delta\tilde{H}^{(0)}\cdot\left(\tilde{\rho},\tilde{T}\right)\right]. \tag{23}$$

The calculation of entropy is carried out by analog relationship. Comparison with H and S data and results of work [25] show that generalised crossover equation of state reliably define thermal and caloric properties of n-alcanes in the range of given parameters $\left|\Delta\tilde{\rho}\right| \le 0.6$; $\tau_s \le \tau \le 1.25$.

So, we can conclude that the application of Lee and Kesler generalised equation of state [14] and generalised crossover equation of state permits to predict reliably caloric properties in liquid and gas phases including critical region.

Table 1. Values of coefficients of equation (8) & standart desviations (SD), %

Coefficients of equation (8)	Enthalpy				Entropy				Enthalpy of vapourisation			
	$\Delta\widetilde{F} = \frac{H^0 - H^{'} - \Delta H_c}{RT_c}\tau^{1/2}$				$\Delta\widetilde{F} = \frac{S^0 - S^{'} - \Delta S_c}{R}\tau$				$\Delta\widetilde{F} = \frac{\Delta H_v}{RT_c}\tau^{1/2}$			
	Variant I	SD	Variant II	SD	Variant I	SD	Variant II	SD	Variant I	SD	Variant II	SD
α_1	1.10785		1.17277		0.97583		0.88151		-2.79988		-2.75395	
α_2	-2.67043	1.07	-2.8178	1.23	-2.76186	1.58	-2.70911	1.75	-3.93361	0.88	-4.03734	0.89
α_3	2.53574		2.47914		2.14024		2.12887		8.15593		8.11450	
α_4	5.00552		6.78465		3.76324		5.94999		0.42397		1.60811	
α_5	-2.99824		-2.93284		-1.84408		-2.61386		-3.28427		-3.15363	
α_6	2.96450		3.01214		3.38216		3.21044		8.21302		8.21257	
α_7	4.48634		0		3.60179		0		2.96950		0	
β_0	0.320		0.315		0.297		0.292		0.396		0.395	
β_1	0.289		0.293		0.300		0.300		0.350		0.35	

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APPENDIX

1. Symbols of the dimensionless thermodynamic Values:

$$\left.\begin{array}{l}\tilde{T} = -T_c/T,\quad \Delta\tilde{T} = 1 - T_c/T,\quad \Delta\tilde{\rho}=\rho/\rho_c - 1,\\ \tilde{\mu} = \mu\rho_c T_c/Tp_c,\quad \Delta\tilde{\mu} = \tilde{\mu} - \mu_0(\Delta\tilde{T}),\quad \tilde{p}=pT_c/p_cT,\\ \tilde{A} = \rho A T_c/Tp_c,\quad \tilde{U} = \rho U/p_c,\quad \tilde{S} = \rho S T_c/p_c,\quad \tilde{H}=\rho\cdot HT_c/Tp_c\\ \tilde{X} = \left[\partial\tilde{\rho}/\partial\tilde{\mu}\right]_T,\ \tilde{C}_v = \rho\cdot C_v T_c/p_c,\ \tilde{C}_p = \rho\cdot C_p T_c/p_c,\ \tilde{W} = W\left[\rho_c T_c/p_c T\right]^{1/2}\end{array}\right\} \quad (A.1)$$

were: T - temperature, ρ - dencity, μ - chemical potential, P - pressure,

A - helmholtz free-energy, U - internal energy, H - enthalpy,

S -entropy, C_v - isochoric heat capacity, C_p - isobaric heat capacity,

W - sound velocity.

2. The thermodynamic relationship

$$\tilde{P} = \tilde{\rho}\tilde{\mu} - \tilde{A} \quad (A.2)$$

$$\tilde{S} = -\tilde{T}\tilde{U} - \tilde{A}, \quad (A.3)$$

$$\tilde{H} = \tilde{\rho} - \tilde{T}\tilde{U}, \quad (A.4)$$

3. The fundamental equation of state is

$$\tilde{A} = \tilde{\rho}\mu_0\left(\Delta\tilde{T}\right) + \tilde{A}_0\left(\Delta\tilde{T}\right) + \Delta\tilde{A}_0, \quad (A.5)$$

were: $$\tilde{A}_0\left(\Delta\tilde{T}\right) = -1 + \sum_{j=1}^{4} A_j\left(\Delta\tilde{T}\right)^j, \quad (A.6)$$

$$\mu_0\left(\Delta\tilde{T}\right) = \sum_{j=0}^{4} m_j\left(\Delta\tilde{T}\right)^j, \quad (A.7)$$

4. The thermodynamic derivatives are

$$\tilde{\mu} = \left(\frac{\partial\Delta\tilde{A}}{\partial\Delta\tilde{\rho}}\right)_{\Delta\tilde{T}}, \quad (A.8)$$

$$\left(\tilde{X}\right)^{-1} = \left(\frac{\partial^2\Delta\tilde{A}}{\partial\left(\Delta\tilde{\rho}\right)^2}\right)_{\Delta\tilde{T}}, \quad (A.9)$$

$$\tilde{U} = -\frac{\partial \tilde{A}_0(\Delta\tilde{T})}{\partial \Delta\tilde{T}} - \tilde{\rho}\,\frac{\partial \tilde{\mu}_0(\Delta\tilde{T})}{\partial \Delta\tilde{T}} - \left(\frac{\partial \Delta\tilde{A}}{\partial \Delta\tilde{T}}\right)_{\Delta\tilde{\rho}}, \tag{A.10}$$

$$\tilde{W} = \left(\frac{\tilde{\rho}\,\tilde{C}_p}{\tilde{X}\,\tilde{C}_v}\right)^{1/2}. \tag{A.11}$$

5. The fundamental crossover equation of State

$$M = c_\rho\left(\Delta\tilde{\rho} - B_3\Delta\tilde{T}\right) + c\left(\frac{\partial \Delta\tilde{A}_r}{\partial t}\right)_M, \tag{A.12}$$

$$t = c_t\Delta\tilde{T} + \left(\frac{\partial \Delta\tilde{A}_r}{\partial M}\right)_t, \tag{A.13}$$

$$\Delta\tilde{A} = \Delta\tilde{A}_r - c\left(\frac{\partial \Delta\tilde{A}_r}{\partial M}\right)_t\left(\frac{\partial \Delta\tilde{A}_r}{\partial t}\right)_M, \tag{A.14}$$

$$\begin{aligned}\Delta\tilde{A}_r &= 1/2tM^2\Gamma Д + 1/4!u\Lambda M^4 Д^2 U + 1/5!\alpha_{05}M^5 Д^{5/2}\gamma U + \\ &+ 1/6!\alpha_{06}M^6 Д^3 U^{3/2} + 1/4!\alpha_{14}tM^4\Gamma Д^2 U^{1/2} + \\ &+ 1/2!2!\alpha_{22}t^2M^2\Gamma^2 Д\, U^{-1/2} - 1/2t^2\Re,\end{aligned} \tag{A.15}$$

were: $\Gamma = Y^{(2-1/\nu)/\omega}$, (A.16)

$Д = Y^{-\eta/\omega}$, (A.17)

$\gamma = Y^{(2\omega_3-1)/2\omega}$, (A.18)

$U = Y^{1/\omega}$, (A.19)

$\Re = \nu/\alpha\bar{u}\Lambda\left(Y^{-\alpha/\nu\omega} - 1\right)$, (A.20)

The crossover function Y is determined by relationship

$$(1 - \bar{u})\,Y = \bar{u}\,[1 + (\Lambda/k)^2]^{1/2}\,Y^{1/\omega}, \tag{A.21}$$

were: $k^2 = t\Gamma + 1/2\,u\Lambda U M^2 Д$, (A.22)

$\tilde{u} = u/u^*$. (A.23)

6. The first thermodynamic derivatives are

$$\left(\frac{\partial \Delta \tilde{A}}{\partial \Delta \tilde{\rho}}\right)_{\Delta \tilde{T}} = c_\rho \left(\frac{\partial \Delta \tilde{A}_r}{\partial M}\right)_t, \tag{A.24}$$

$$\left(\frac{\partial \Delta \tilde{A}}{\partial \Delta \tilde{T}}\right)_{\Delta \tilde{\rho}} = c_t \left(\frac{\partial \Delta \tilde{A}_r}{\partial t}\right)_M - c_\rho B_3 \left(\frac{\partial \Delta \tilde{A}_r}{\partial M}\right)_t, \tag{A.25}$$

7. The derivatives of the crossover funtion are

$$\left(\frac{\partial k^2}{\partial t}\right)_M = F_1(t, M)\Gamma, \tag{A.26}$$

$$\left(\frac{\partial k^2}{\partial M}\right)_t = F_1(t, M)u\Lambda M^2 U Д, \tag{A.27}$$

$$\left(\frac{\partial Y}{\partial t}\right)_M = F_2(t, M)\Gamma, \tag{A.28}$$

$$\left(\frac{\partial Y}{\partial M}\right)_t = F_2(t, M)u\Lambda U Д, \tag{A.29}$$

were: $F_1 = (1 + f_1 f_2)^{-1}$ (A.30)

$$F_2 = f_1 Y F_1, \tag{A.31}$$

$$f_1 = \frac{\Lambda}{2k^4}\left(1 + \frac{\Lambda^2}{k^2}\right)^{-1}\left[\frac{1}{\omega} + \frac{(1-\tilde{u})Y}{1-(1-\tilde{u})Y}\right]^{-1}, \tag{A.32}$$

$$f_2 = -\left[\left(\frac{2-\nu^{-1}}{\omega}\right)t\Gamma + \left(\frac{1-\eta}{2\omega}\right)u\Lambda M^2 U Д\right], \tag{A.33}$$

8. Universal Critical-Region Constants

$\nu = 0.630$

$\eta = 0.0333$

$\alpha = 2 - 3\nu = 0.110$

$\Delta = 0.51$

$\omega = \Delta/\nu = 0.80952$

$\omega_s = 2.1$

$u^* = 0.472$

Table A.1 Parametrs of the Generalized Crossover Equation of State.

Parametrs	Symbol	Values for	
		a simple substance	a standart substance
Critical parametrs	T_c, K	150.66	507.20
	P_c, MPa	4.860	3.025
	ρ_c, kg m^{-3}	530.9	233.5
Parametrs of the crossover function	$\bar{u}$	0.549	0.448
	λ	1.9799	1.301
Parametrs of the asymmetric real fluid	C	- 0.04741	- 0.0150
	C_t	1.9996	2.189
	C_p	2.35231	2.360
	B_3	- 0.2641	- 0.320
Coefficients of the Landau expansion	a_{05}	- 0.45710665	- 0.412673
	a_{06}	0.50481024	1.476329
	a_{14}	0.01504220	0.446138
	a_{22}	- 0.02229074	0.359876
Coefficients of the regular thermal function $\tilde{A}_0(\Delta\tilde{T})$	A_0	- 1.0	- 1.0
	A_1	- 4.8228248	-6.524805
	A_2	3.9067660	2.324301
	A_3	- 5.9100274	16.758295
	A_4	16.424060	- 50.8426695
Coefficients of the regular thermal function $\tilde{\mu}_0(\Delta\tilde{T})$	m_0	6.2675	- 104.093
	m_1	- 37.462	- 84.527
	m_2	- 6.62385	- 55.0411
	m_3	2.21443	- 46.1598
	m_4	- 15.58372	- 29.8779

FIGURE CAPTIONS

Fig.1. Thermodynamic calculation diagram of caloric properties:

- calculation by local equation of state;
- calculation by numerical integration of C_p-data;
- calculation by equation of state Lee and Kesler [14].

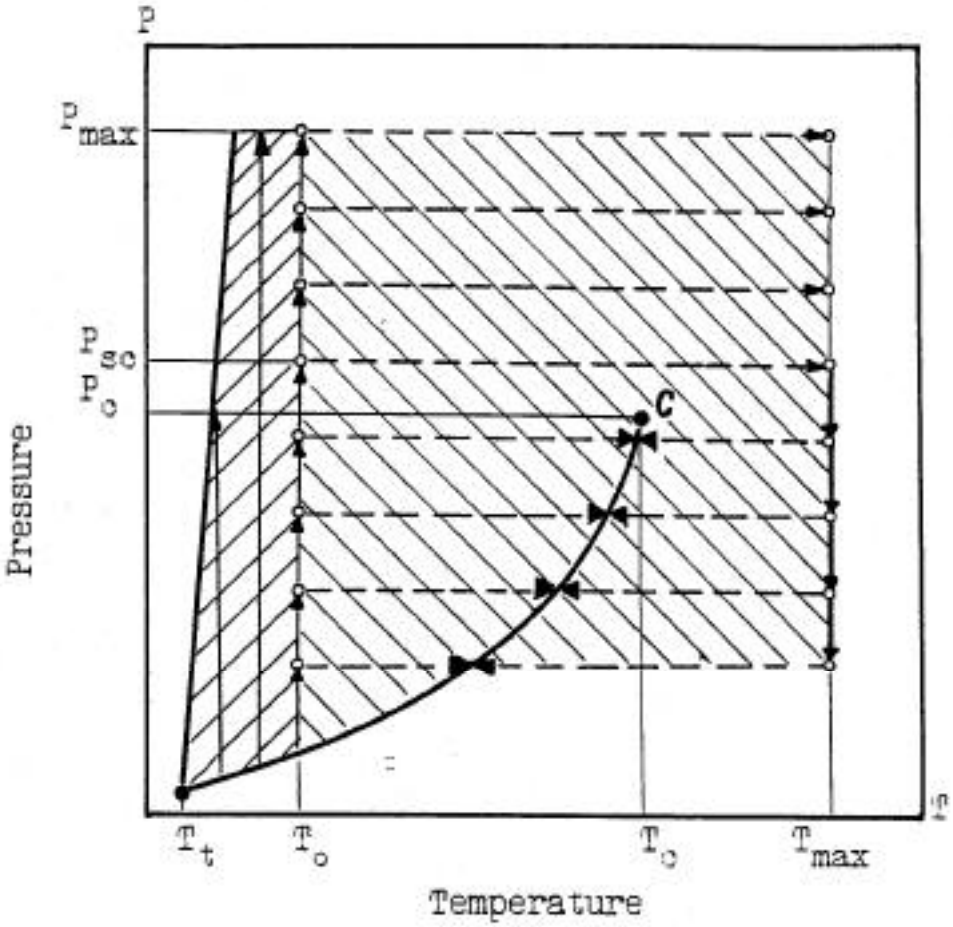
Fig.2. The configuration enthalpy ΔH_c and entropy ΔS_c in the critical Point of the n-alcanes as a function of the Pitzer acentric factor ω.

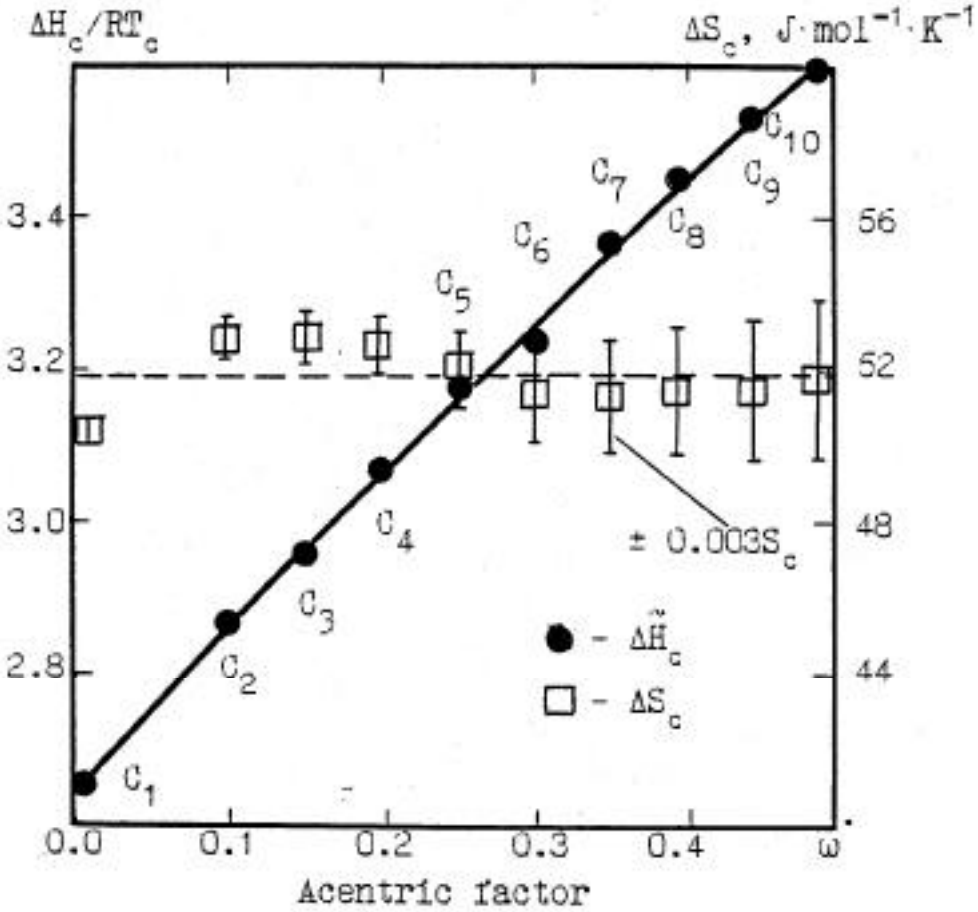
Fig.3. Deviations between the calculated values of the enthalpy and the experimental values: 1 - methane; 2 - ethane; 3 - propane; 4 - n-butane; 5 - n-pentane; 6 - n-hexane; 7 - n-heptane; 8- n-octane; 9- n-nonane; 10 -n-decane.

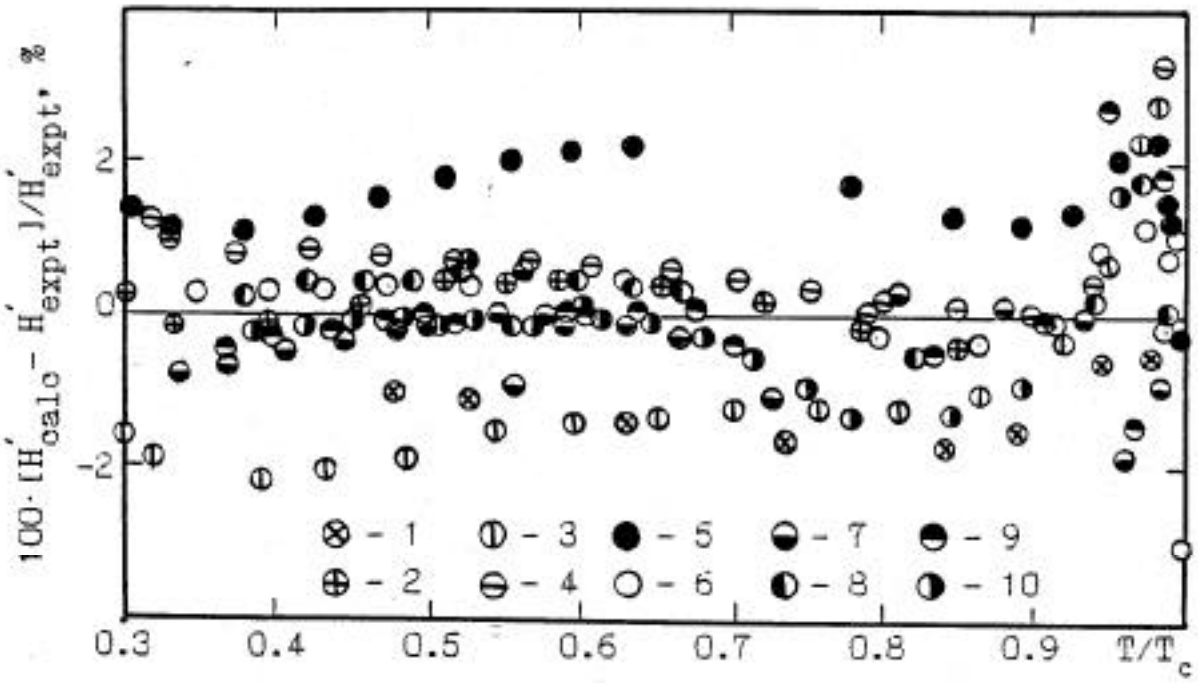
Fig.4. Deviations between the calculated values of the entropy and the experimental values:

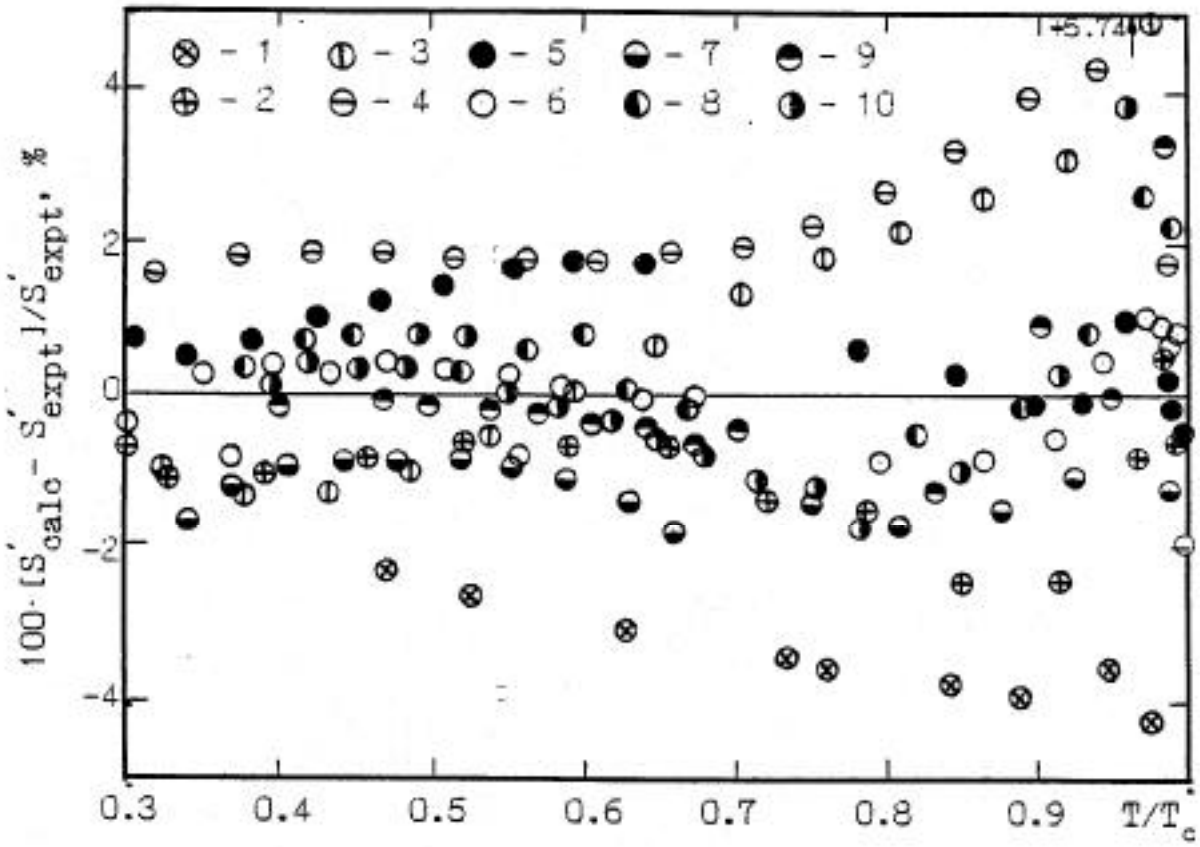
1 - methane; 2 - ethane; 3 - propane; 4 - n-butane; 5 - n-pentane; 6 - n-hexane; 7 - n-heptane; 8- n-octane; 9- n-nonane; 10 -n-decane.

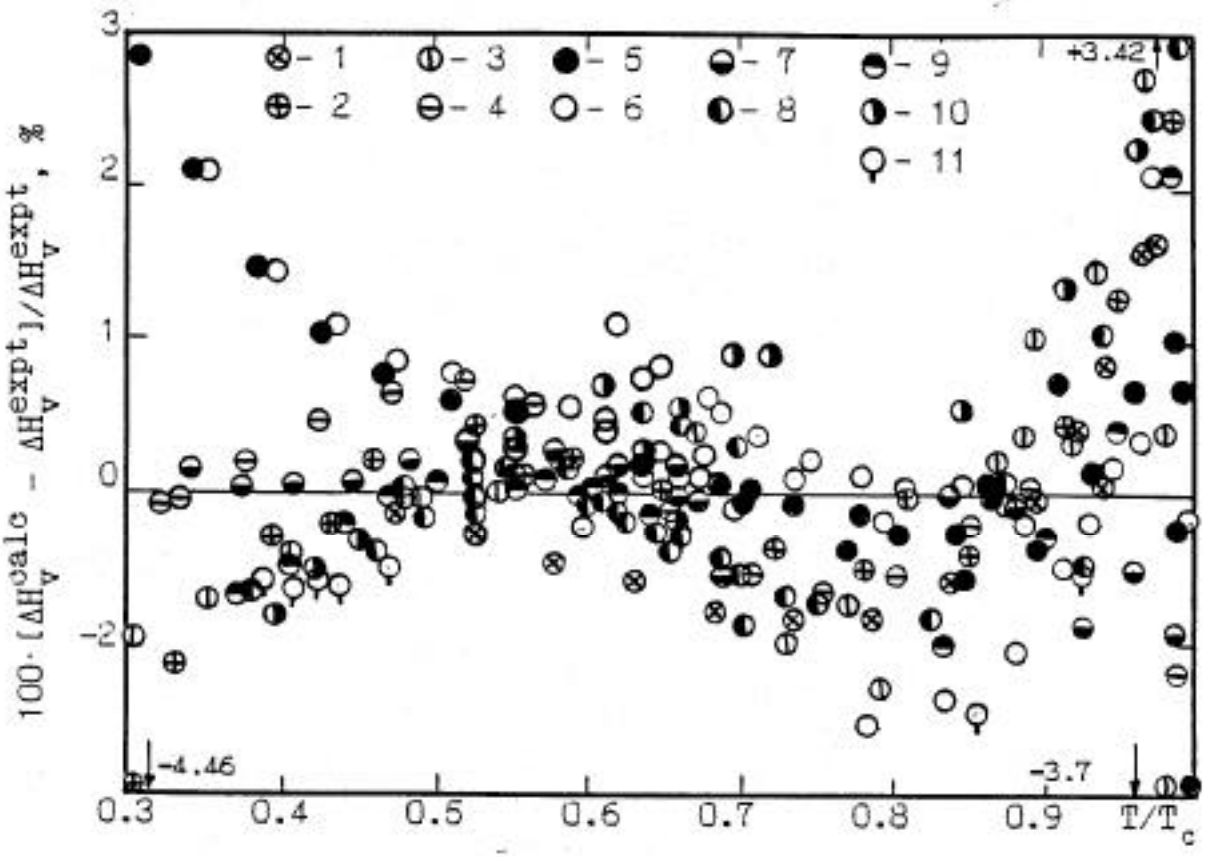
Fig.5. Devications the calculated values of the enthalpy of vapourisation and the experimental values: 1- methane; 2 - ethane; 3 - propane; 4 - n-butane; 5 -n-pentane; 6 - n-hexane; 7 - n-heptane; 8 - n-oktane; 9 - n-nonane; 10 - n-decane; 11 - n-undecane.


P
P_{max}
P_{sc}
P_c
C
Pressure
T_t
T_o
T_c
T_{max}
T
Temperature


ΔH_c/RT_c
ΔS_c, J·mol^-1·K^-1
3.4
3.2
3.0
2.8
56
52
48
44
C_1
C_2
C_3
C_4
C_5
C_6
C_7
C_8
C_9
C_10
± 0.003S_c
● - ΔH̃_c
□ - ΔS_c
0.0
0.1
0.2
0.3
0.4
ω
Acentric factor


100·[H'calc − H'expt]/H'expt, %
2
0
−2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
T/Tc
- 1
- 2
- 3
- 4
- 5
- 6
- 7
- 8
- 9
- 10


⊗ - 1
⊕ - 2
◐ - 3
⊖ - 4
● - 5
○ - 6
◒ - 7
◐ - 8
◓ - 10
4
2
0
-2
-4
0.3
0.4
0.5
0.6
0.7
0.8
0.9
T/T_c
100·[S'_calc - S'_expt]/S'_expt, %


3
2
1
0
-2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
T/T_c
100·[ΔH_v^calc - ΔH_v^expt]/ΔH_v^expt, %
⊗ - 1
⊕ - 2
⦶ - 3
⊖ - 4
● - 5
○ - 6
◒ - 7
◐ - 8
◓ - 9
◑ - 10
♀ - 11
+3.42
-4.46
-3.7