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ANTISYMMETRY OF THE EXPERIMENTALLY DETERMINED CHEMICAL POTENTIAL OF REAL GASES AND THOM'S THEORY OF CATASTROPHES

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Abstract: The observed antisymmetry of the chemical potential $\mu(\varrho, T)$ of real gases around the critical density ϱ_c and Thom's theory of catastrophes suggested that the following two hypotheses be tested against experimental data:

a) $\partial^4\mu(\varrho_c, T)/\partial\varrho^4 = 0$ and $\partial^2\mu(\varrho_c, T)/\partial\varrho^2 = 0$ for all T, and

b) $\partial^2\mu(\varrho_c, T)/\partial\varrho^2 = 0$ for all T.

We found that the hypotheses a) and b) are compatible with experimental data for Xe, CO_2, N_2, ethylene and propene, if the experimental $P/RT\varrho$ values are changed, on the average, by about 0.2% and 0.05%, respectively.

1. Introduction

Edwards and Woodbury[1] in attempting to describe their measurements of densities of saturated ^{4}He near its critical point by the first two terms of the Landau-Lifshitz expansion

$$N^{-1}(\partial^2F/\partial v^2)_{(T,V)} = -(\partial P/\partial v)_T = A(T - T_c) + B(v - v_c)^2, \qquad (1)$$

where $F = F(T, V, N)$ is the Helmhotz free energy, $v = V/N$ is the molar volume and A and B are adjustable positive constants, found it necessary to add two more terms to the right hand side of (1). Closer examination of their expression by Tisza and Chase[2] brought out that it leads to inconsistencies when applied at points away from the coexistence curve. Further Tisza and Chase[2] pointed out that these difficulties may be effectively avoided by using only the first two terms of an analogous Landau-Lifshitz expansion

$$V^{-1}(\partial^2F/\partial\varrho^2)_{T,V} = (\partial\mu/\partial\varrho)_T = \alpha(T - T_c) + \beta(\varrho - \varrho_c)^2, \tag{2}$$

where μ is the chemical potential, V is fixed, $\varrho = N/V$ and $\alpha, \beta > 0$ are two adjustable constants (cf. also Chase and Williamson[3]). They concluded therefore, that the antisymmetry of the chemical potential μ as a function of $(\varrho - \varrho_c)$ for $\varrho \sim \varrho_c$ may be a fundamental property of real gases, at least in the vicinity of the critical temperature T_c.

On numerically integrating the relation

$$\mu(P, T) = \mu(P_0, T) + \int_{P_0}^{P} V\,\mathrm{d}P \tag{3}$$

using experimental data for CO_2, Ar and ^4He, Vicentini-Missoni, Levelt Sengers and Green[4] and Levelt Sengers[4] have obtained diagrams of the chemical potential versus density ϱ at different temperatures. These diagrams indicate that the plots of the chemical potential μ as a function of $(\varrho - \varrho_c)$ look antisymmetric over a range of densities up to nearly 50 percent from critical, and up to temperatures far above the critical. Consequently, these results confirm the hypothesis of Tisza and Chase[1] about the antisymmetry of the chemical potential.

Detailed investigation of the critical region of ^3He, ^4He, Xe, CO_2 and H_2O revealed that also within the critical region the chemical potential μ as a function of $\Delta\varrho = (\varrho - \varrho_c)$ displays a high degree of antisymmetry, described as follows

$$\Delta\mu = a\,\Delta\varrho\,(|\Delta\varrho|^{\delta-1} - b\,\Delta\varrho\,|\Delta\varrho|^{\epsilon-2}), \tag{4}$$

where $\delta \approx 4.2 - 5$ and $\epsilon \approx 6$ (cf. Green, Vicentini-Missoni, Levelt-Sengers[6] Vicentini-Missoni, Levelt-Sengers and Green[7], Wallace and Meyer[8], Vicentini-Missoni[9], Kirestead[10], Levelt-Sengers[11]) so that

$$\frac{\partial\mu}{\partial\varrho} = \frac{\partial^2\mu}{\partial\varrho^2} = \frac{\partial^3\mu}{\partial\varrho^3} = \frac{\partial^4\mu}{\partial\varrho^4} = 0 \text{ for } T = T_c \text{ and } \varrho = \varrho_c \tag{5}$$

(cf. also Habgood and Schneider[12]; Widon and Rice[13]; Martin[14]).

The chemical potential, say μ_{lg}, associated with the lattice gas model of fluids having a particle-hole symmetry, has been shown to be an exactly antisymmetric function of $(\varrho - \varrho_c)$ for all temperatures $T > T_c$, so that $\partial^n\mu_{lg}(\varrho_c, T)/\partial\varrho^n = 0$ for any even n (cf. Lee and Yang[15]). And it has been pointed out by Widon[16] that some traces of this complete antisymmetry of the chemical potential μ_{lg} should be displayed also by real fluids near the critical point.

It has been shown by Ribarič and Žekš[17] that the chemical potential, say $\mu_w(\varrho, T)$ associated with the Van der Waals equation does exhibit cusp catastrophe*, thereby showing the following antisymmetry

$$\frac{\partial^2 \mu_w(\varrho_c, T)}{\partial \varrho^2} \equiv 0, \quad \frac{\partial^4 \mu_w(\varrho_c, T)}{\partial \varrho^4} \neq 0 \text{ for all } T, \tag{6}$$

and

$$\frac{\partial \mu_w(\varrho_c, T)}{\partial \varrho} = 0 \text{ for } T = T_c \text{ and } \frac{\partial^3 \mu_w(\varrho_c, T)}{\partial \varrho^3} > 0 \text{ for all } T. \tag{7}$$

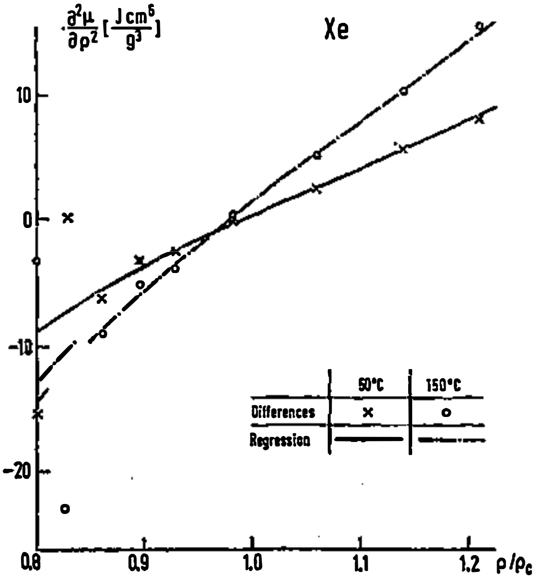

Fig. 1. Second derivatives of the chemical potential of Xe for $T = 50$ °C and $T = 150$ °C as obtained from experimental data: i) on applying Equ (11) (50 °C crosses, 150 °C dots); ii) obtained via polynominal regression (50 °C —, 150 °C — · — · —).

Furthermore, the zeros, say ϱ_n of even derivatives of the chemical potential $\mu_w(\varrho, T)$ do not depend on temperature and satisfy the following equation

$$3n = (\varrho_n/\varrho_c)(3\varrho_c/\varrho_n - 1)^{n+1} + \varrho_n/\varrho_c - 3, \; n \text{ even, i. e.}$$

$$\partial^n \mu_w(\varrho_n, T) / \partial \varrho^n = 0.$$

So it is not difficult to show that all even zeros $\varrho_n \in [\varrho_c, 1.5\,\varrho_c]$ and that $\varrho_n \to 1.5\,\varrho_c$ as $n \to \infty$; in particular $\varrho_4 = 1.1318$, $\varrho_6 = 1.2040$, $\varrho_8 = 1.2503$,

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*) For the applicability of Thom's[18] theory of catastrophes see Schulman and Revzen[19].

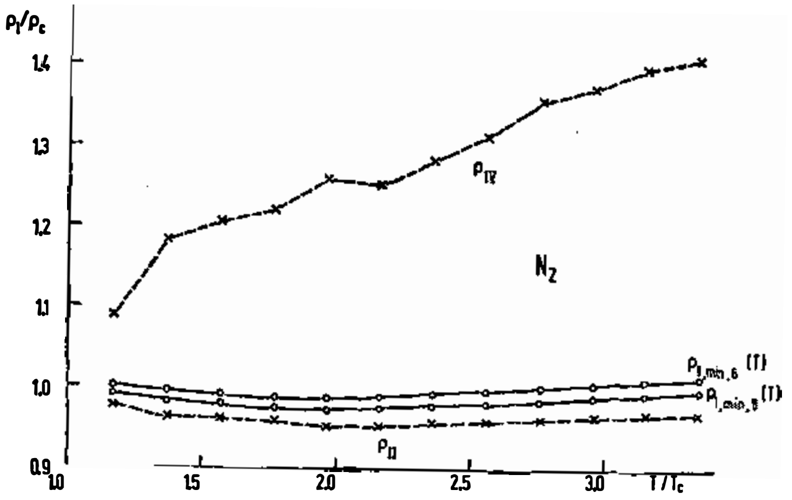

Fig. 2. Zeros ϱ_{II} and ϱ_{IV} of the second and fourth derivatives of the chemical potential μ_{N2} as functions of the reduced temperatures T/T_c. Full lines give that position of the assumed common zero $\varrho_{1,min,n}$ of $\partial^2 \mu_{N2}/\partial\varrho^2$ and $\partial^4 \mu_{N2}/\partial\varrho^4$ which ensures the best fit of the ansatz (13) with $n = 6$ and $n = 8$ for N_2 experimental data with densities $\varrho \in [0,2\, \varrho_c]$, cf. Fig. 3.

Furthermore, Ribarič and Žekš[17)], have pointed out that the empirical formulas used for fitting of experimental PVT data in the liquid and gaseous region of propylene, ethylene, N_2, O_2, liquid xenon, liquid argon and methane indicate that associated μ, ϱ, T surfaces would, at the critical point in the absence of fluctuations, exhibit cusp or butterfly catastrophe, i. e. were it not for fluctuations, we would have either

$$\frac{\partial^2\mu}{\partial\varrho^2} \equiv 0 \text{ for all } T \text{ at } \varrho = \varrho_c, \text{ and} \frac{\partial^3\mu}{\partial\varrho^3} \neq 0 \text{ and} \frac{\partial\mu}{\partial\varrho} = 0 \text{ at } T = T_c, \varrho = \varrho_c, \tag{8}$$

or

$$\frac{\partial^4\mu}{\partial\varrho^4} \equiv 0 \text{ for all } T \text{ at } \varrho = \varrho_c, \text{ and} \frac{\partial^5\mu}{\partial\varrho^5} \neq 0 \text{ and } \frac{\partial^3\mu}{\partial\varrho^3} = \frac{\partial^2\mu}{\partial\varrho^2} = \frac{\partial\mu}{\partial\varrho} = 0 \text{ at } T = T_c, \ \varrho = \varrho_c. \tag{9}$$

Result (5), however seems to rule out the first possibility, leaving butterfly catastrophe for which possibly also $\partial^2 \mu(\varrho_c, T)/\partial\varrho^2 = 0$ for all T, cf. Ribarič and Žekš[17)], Fig. 2.

2. *Analysis of real-gas data and discussion*

If we assume that the chemical potential $\mu(\varrho, T)$ of real gases is an analytic function of density ϱ, then its antisymmetry around the line $\varrho = \varrho_c$ can be adequately quantitatively described by the number of even derivatives $\partial^n \mu(\varrho, T)/\partial \varrho^n$ ($n = 2, 4, 6, \ldots$), which equal zero at $\varrho = \varrho_c$ for all temperatures T. In what follows, we intend therefore to investigate the antisymmetry of the chemical potential μ of some real gases along the non-critical isotherm by determining its derivatives $\partial^n \mu/\partial \varrho^n$ from experimental data:

— directly by numerical differentiation, and

— indirectly via polynomial regression.

To this end we will analyse data measured by Michels and Michels$^{20)}$ and Michels, Michels and Wouters$^{21)}$ on CO_2; Michels, Lunbeck and Wolkers$^{22)}$ on N_2; Michels, Wassenaar and Louwerse$^{23)}$ on Xe; Michels, Wassenaar, Louwerse, Lunbeck and Wolkers$^{24)}$ on propene; Trappeniers, Wassenaar and Wolkers$^{25)}$ on ethylene.

From (3) we deduce the following approximation for the first derivative of the chemical potential

$$\left(\frac{\partial \mu\left(\frac{\varrho_i + \varrho_{i+1}}{2}, T\right)}{\partial \varrho}\right)_T = \frac{1}{\varrho}\left(\frac{\partial P}{\partial \varrho}\right)_T \approx \left(\frac{\partial \mu\left(\frac{\varrho_i + \varrho_{i+1}}{2}, T\right)}{\partial \varrho}\right)_{ap} \equiv$$
$$\equiv \frac{2}{\varrho_{i+1} + \varrho_i}\,\frac{P_{i+1} - P_i}{\varrho_{i+1} - \varrho_i}, \tag{10}$$

and analogously

$$\left(\frac{\partial^n \mu\left(\frac{\varrho_j + \varrho_{j+1}}{2}, T\right)}{\partial \varrho^n}\right)_T \approx \left(\frac{\partial^n \mu\left(\frac{\varrho_j + \varrho_{j+1}}{2}, T\right)}{\partial \varrho^n}\right)_{ap} \equiv$$
$$\equiv \frac{1}{\varrho_{j+1} - \varrho_j}\left[\left(\frac{\partial^{n-1} \mu(\varrho_{j+1}, T)}{\partial \varrho^{n-1}}\right)_{ap} - \left(\frac{\partial^{n-1} \mu(\varrho_j, T)}{\partial \varrho^{n-1}}\right)_{ap}\right] \tag{11}$$

for higher derivatives $n = 2, 3, \ldots$, where $P_i \varrho_{i,j}$ are experimentally determined values of pressure and the corresponding density. On applying formulas (10) and (11) to the experimental data for Xe, we obtained approximate derivatives of the associated chemical potential. In Fig. 1 the obtained approximate values of the second derivative $\partial^2 \mu(\varrho, T)/\partial \varrho^2$ are given for two isotherms at 50 °C and 150 °C. It turned out that the approximations to the higher derivatives, third, fourth ans so on, could not be well obtained directly by (11) due to experimental errors. Therefore, we determined the polynomial approximations to $P = P(\varrho)$ by regression analysis, and then calculated from the obtained virial expansion the first seven derivatives

$$\frac{\partial^n \mu(\varrho, T)}{\partial \varrho^n} = \frac{\partial^{n-1}}{\partial \varrho^{n-1}}\left(\frac{1}{\varrho}\,\frac{\partial P(\varrho, T)}{\partial \varrho}\right) \tag{12}$$

of the chemical potential. In Fig. 1 the second derivatives of the chemical potential of xenon, say μ_{Xe}, are given for two isotherms $T = 50$ °C and $T = 150$ °C as calculated by polynomial regression over the whole range $(0 \leq \varrho \leq 2.746\ \varrho_c)$ of experimental data for Xe using polynomials of 8^{th} order. Fig. 1 indicates that the zeros, say $\varrho_{II}(T)$ of the second derivative $\partial^2 \mu_{Xe}(\varrho, T)/\partial\varrho^2$ approximately

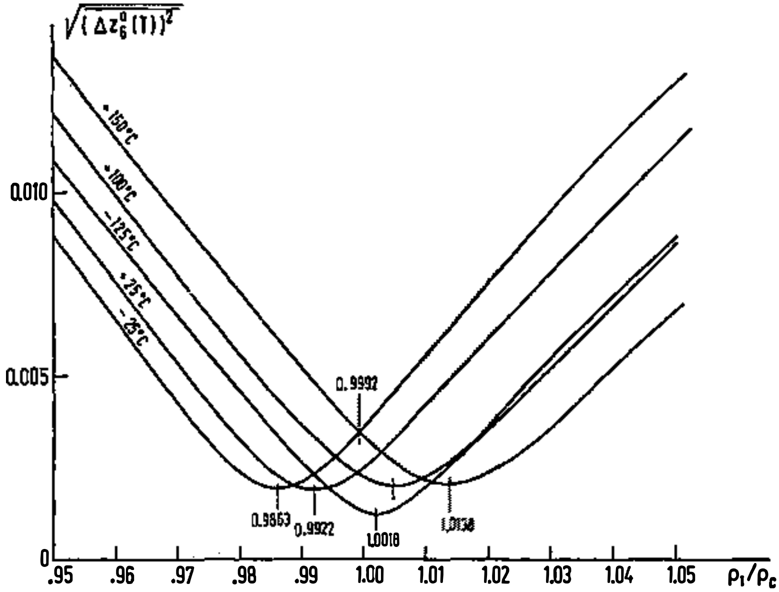

Fig. 3. The average change $\sqrt{(\Delta z_6^q(T))^2}$ of experimental data $z_t = P_l/RT$ for N_2 required to bring them into accordance with hypothesis (a) at $\varrho = \varrho_1$ as function of ϱ_1/ϱ_c for five isotherms. Full vertical lines indicate positions of $\varrho_{1,min,3}(T)$ plotted on Fig. 2. Dotted vertical line indicates $\varrho_1 = 0.9992\ \varrho_c$ which minimizes $\max\limits_{T} \sqrt{(\Delta z_6^q(T))^2}\,(\varrho_1)$ making it equal to 0.0035.

equal ϱ_c for $T = 50$ °C and $T = 150$ °C. Using experimental data with $\varrho \in [0{,}2\ \varrho_c]$ we have calculated the first seven derivatives of the associated chemical potential from the 6^{th}, 7^{th} and 8^{th} order virial expansions for Xe, CO_2, N_2, ethylene and propene. For N_2 the zeros, say ϱ_{II}, of the second derivative $\partial\, \mu_{N2}/\partial\varrho^2$ and zeros, say ϱ_{IV}, of the fourth derivative $\partial^4\mu_{N2}/\partial\varrho^4$ are plotted as functions of the reduced temperature T/T_c on Fig. 2 as obtained from the sixth order virial expansion. The results for Xe, CO_2, ethylene and propene are similar. Fig. 2 shows that $\varrho_{II} \approx \approx \varrho_{IV} \approx \varrho_c$ at $T \approx T_c$, thereby the zeros, say ϱ_{VI}, of the sixth derivative $\partial^6\,\mu/\partial\varrho^6$ do not seem to tend to ϱ_c as T tends to T_c, all in agreement with relations (5). As the reduced temperature increases, ϱ_{II} and ϱ_{IV} move apart. Thereby ϱ_{II} decreases to about 5% below ϱ_c whereas ϱ_{IV} is steadily increasing up to 40% above ϱ_c at $T/T_c = 3.5$.

Let us say that the experimentally determined chemical potential $\mu(\varrho, T)$ has n-th order antisymmetry around the line $\varrho = \tilde{\varrho}_c$ if all even derivatives

$\partial^j \mu (\varrho_c, T)/\partial \varrho^j$ up to $2n$-th order are identically equal to zero for all temperatures. So the chemical potential μ_w associated with Van der Waals equation has asymmetry of the first order around the line $\varrho = \tilde{\varrho}_c = \varrho_{cw}$. The temperature dependence of ϱ_{II} and ϱ_{IV} as given in Fig. 2 and the graphical inspection of experimentally determined values of the chemical potential $\mu (\varrho, T)$ of CO_2, Ar and ^{4}He obtained by Vicentini-Missoni, Levelt-Sengers and Green[7)] suggest that the chemical potential of real gases could, with reasonable accuracy, exibit an antisymmetry of at least first order around the line $\varrho = \tilde{\varrho}_c \sim \varrho_c$. Therefore, let us put forward two hypotheses:

a) the chemical potential $\mu (\varrho, T)$ of real gases has antisymmetry of the second order around $\varrho = \tilde{\varrho}_c$, i. e. there is a constant, say $\tilde{\varrho}_c$, such that $\varrho_{II} = \varrho_{IV} = \tilde{\varrho}_c$ for all temperatures $T > T_c$; and

b) this antisymmetry is only of the first order, i. e., there is a constant, say $\tilde{\varrho}_c$ such that $\tilde{\varrho}_{II} = \tilde{\varrho}_c$ for all T.

Let us first test hypothesis a) on its compatibility with experimental data by trying to estimate how much the experimental data have to be altered so as to make it true. To this end we take the following specialised polynominal ansatz

$$z_n^a (\varrho, T, \varrho_1) \equiv c_0 \left[1 - \frac{2}{3} (\varrho/\varrho_1)^2 + \frac{1}{5} (\varrho/\varrho_1)^4\right] + c_1 \varrho + c_3 \Big(\varrho^3 - \frac{8}{3} \varrho_1 \varrho^2\Big) + \sum_{i=5}^{n} c_i \Big\{ \frac{1}{6} (i+1)(i-1)[(i-2)(i-3) - 2] \varrho_1^{i-2} \varrho^2 - \frac{1}{30} (i+1)(i-1)(i-2)(i-3) \varrho_1^{i-4} \varrho^4 + \varrho_i \Big\}, \tag{13}$$

such that

$$\left.\frac{\partial^2 \mu_n (\varrho, T, \varrho_1)}{\partial \varrho^2}\right|_{\varrho=\varrho_1} = \left[\frac{\partial}{\partial \varrho} \frac{1}{\varrho} \frac{\partial (RT \varrho\, z_n^a (\varrho, T, \varrho_1))}{\partial \varrho}\right]_{\varrho=\varrho_1} = 0 \text{ and } \quad \left.\frac{\partial^4 \mu_n (\varrho, T, \varrho_1)}{\partial \varrho^4}\right|_{\varrho=\varrho_1} = 0, \tag{14}$$

where c_0, c_1, c_3 and c_n are temperature dependent constants to be determined by linear regression from experimental data $z_l = P_l/RT \varrho_l$ for various values of the parameter $\varrho_1 \geq 0$. Expression (13) is obtained from a general polynomial ansatz on eliminating constants c_2 and c_4 by requiring it to satisfy conditions (14).

On choosing values between 0 and $2\varrho_c$ for parameter ϱ_1, we observe that the sum of the squares of residuals from the regression, say $\sum_i \text{res}_i^2$, as a function of parameter ϱ_1 does have for each isotherm a distinct minimum at, say $\varrho_{1min}(T)$, such that $\varrho_{1min}(T) \sim \varrho_c$ for any temperature. For N_2 experimental data, the values of $\varrho_{1,min}(T)$ are given in Fig. 2 as obtained by applying 6th and 8th order polynomials $z_6^a(\varrho, T, \varrho_1)$ and $z_8^a(\varrho, T, \varrho_1)$. In Fig. 3 we have plotted the average residuals

$$\sqrt{(\Delta z_n^a(T))^2}\,(\varrho_1) = [(\sum_i \mathrm{res}_i^2)/(\text{number of data})]^{1/2} \qquad (15)$$

as obtained from experimental data for N_2 when $n = 6$ for five different isotherms $T = 150$ °C, 100 °C, 25 °C, $-$ 25°C, -125 °C. The value of $\sqrt{(\Delta z_n^a(T))^2}\,(\varrho_1)$ tells us how much on the average we have to change the experimental data $z_j = P_j/RT\,\varrho_j$ of isotherm T in order to be able to fit them exactly with the n^{th} order polynomials satisfying (14) at $\varrho = \varrho_1$ and so yielding a chemical potential such that its second and fourth derivatives both have zero at $\varrho = \varrho_1$. In Fig. 4 we have plotted the

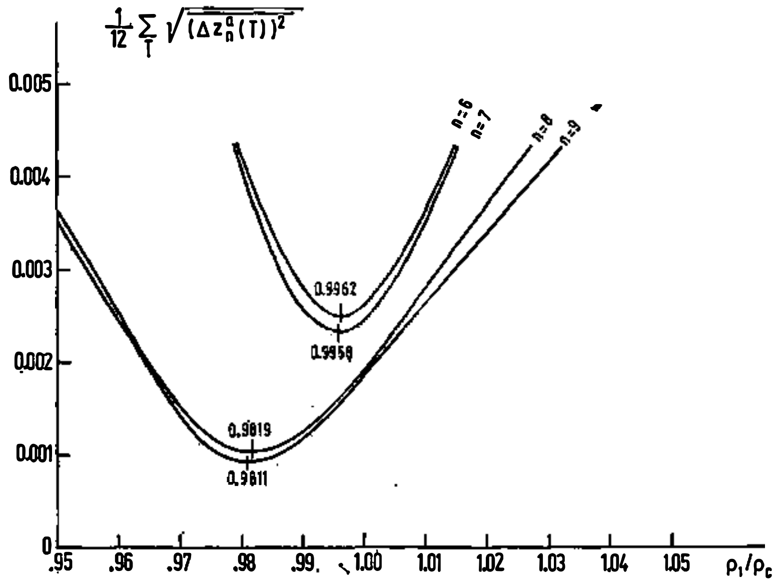

Fig. 4. The values of $\sqrt{(\Delta z_n^a(T))^2}$ averaged over twelve isotherms $T = -125$ °C, -100 °C -75 °C, -50 °C, -25 °C 0 °C, $+25$ °C, $+50$ °C, $+75$ °C, $+100$ °C, $+125$ °C and $+150$ °C of N_2 with $\varrho \in [0{,}2\,\varrho_c]$ for four different cases $n = 6, 7, 8, 9$ as functions of ϱ_1/ϱ_c. Vertical lines indicate the values of ϱ_1/ϱ_c which minimize $\frac{1}{12}\sum_T \sqrt{(\Delta z_n^a(T))^2}\,(\varrho_1)$.

values of $\sqrt{(\Delta z_n^a(T))^2}\,(\varrho_1)$ averaged over twelve isotherms ($T = 150$ °C, 125 °C, 100 °C, 75 °C, 50 °C, 25 °C, 0 °C, -25 °C -50 °C, -75 °C, -100 °C, -125 °C) of N_2 for $n = 6, 7, 8$ and 9. The value $\frac{1}{12}\sum_T \sqrt{(\Delta z_n^a(T))^2}\,(\varrho_1)$ tells us that on changing the experimental data of all twelve isotherms on the average by 0.25% [0.1%] we

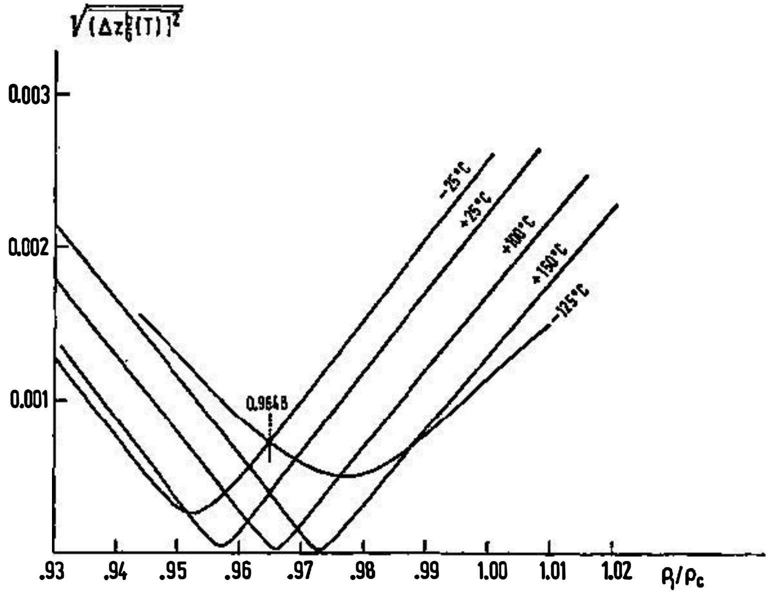

Fig. 5. The average change $\sqrt{(\Delta z_6^b(T))^2}\,(\varrho_1)$ of experimental data $z_i = P_i/RT$ for N_2 necessary to bring them into accordance with hypothesis (b) at $\varrho = \varrho_1$ as a function of ϱ_1/ϱ_c for five isotherms. Dotted vertical line indicates the value $\varrho_1 = 0.9698\,\varrho_c$ which minimizes $\max\limits_T \sqrt{(\Delta z_6^b(T))^2\,(\varrho_1)}$ making it equal to 0.0072.

are able to fit them exactly with 6th [8th] order polynomial (13) such that $\varrho_{II} = \varrho_{IV} = 0.9962\,\varrho_c$ [$0.9819\,\varrho_c$] for all temperatures. Inspection of residuals shows that the maximal change of experimental data z necessary to make z_i's exactly compatible with hypothesis (a) $\partial^4\mu/\partial\varrho^4 = \partial^2\mu/\partial\varrho^2 = 0$ at $\varrho = \bar{\varrho}_c$ for all T when $n = 6$ [$n = 8$] is around 0.7% [0.4%] for all isotherms. So we can say that hypothesis (a) is better then 0.4% compatible with experimental data for N_2 over the whole range of measured densities $\varrho \in [0{,}2\,\varrho_c]$ and for all twelve isotherms between $T = -125$ °C and $T = 150$ °C, because either by increasing the order n of the ansatz (13) used for fitting and/or shortening the density interval of the experimental data to be fitted by (13), the corresponding quantity $\sqrt{(\Delta z_n)_2{}^2}$ can be made substantially smaller.

Analogously, we can investigate the hypothesis (b) that there is $\bar{\varrho}_c$ such that $\varrho_{II} = \bar{\varrho}_c$ for all temperatures but not necessarily $\varrho_{IV} = \bar{\varrho}_c$. To this end we use a specialised polynomial ansatz, say $z_n^b(\varrho, T, \varrho_1)$ analogous to (13) such that only

$$\left.\frac{\partial^2\mu_n(\varrho, T, \varrho_1)}{\partial\varrho^2}\right/_{\varrho=\varrho_1} = \left[\frac{\partial}{\partial\varrho}\frac{1}{\varrho}\frac{\partial(RT\varrho\, z_n^b(\varrho, T, \varrho_1))}{\partial\varrho}\right]_{\varrho=\varrho_1} = 0 \tag{16}$$

for all T. In analogy to Fig. 3 we have plotted in Fig. 5 average residuals, say $\sqrt{(\Delta z_n^b(T))^2}\,(\varrho_1)$ as function of ϱ_1 at which $\partial^2\mu_n/\partial\varrho^2 = 0$ in the case of the sixth order specialised polynomial ansatz ($n = 5$) for five different isotherms. Fig. 5 indicates that the change of experimental data required to make the second derivative of the associated chemical potential equal zero at $\varrho = 0.9648\, \varrho_c$ for all temperatures will result in less than 0.07% change of average residuals $\sqrt{(\Delta z_6^b(T))^2}$ at any temperature $T \in [-125\ °\mathrm{C}, 150\ °\mathrm{C}]$. In Fig. 6 we have plotted the values of $\sqrt{(\Delta z_n^b(T))^2}\,(\varrho_1)$ averaged over the twelve isotherms of N_2 between -125 °C and 150 °C for $n = 6, 7, 8$ and 9. The plotted average value, say $\frac{1}{12} \sum_T \sqrt{(\Delta z_n^b(T))^2}$ (ϱ_1) tells us that on changing the experimental data of all twelve isotherms on the average by 0.45% [0.028%] we are able to fit them exactly with a 6th [8th] order polynomial $z_n^b(\varrho, T, \varrho_1)$ such that $\varrho_{II} = 0.9617\, \varrho_c$ [$0.9600\, \varrho_c$] for all temperatures.

3. *μ, ϱ, T surfaces and Thom's elementary catastrophes*

As explained in the introduction and in the preceding paper by Ribarič and Žekš[17)], hypotheses a) and b) about the antisymmetry of the chemical potential of real gases around the line $\varrho = \varrho_c$, have been suggested by an interpretation of the properties of the chemical potential of a Van der Waals' gas in terms of Thom's theory of catastrophes, by the list of seven elementary catastrophes, and by the experimentally observed antisymmetry of the chemical potential of real gases (a short account of catastrophe theory has been given recently by Zeeman[26)]).

Let us denote by $\Delta\mu$ the difference between the isothermal values at ϱ and ϱ_c of the chemical potential (i. e. of its classical part), so $\Delta\mu = \mu(T, \varrho) - \mu(T, \varrho_c)$. Were the estimated incompatibility ($\sim 0.2\%$) of experimental P, ϱ, T data of the real gases considered with the hypotheses a) effected only by fluctuations and experimental erros, then by hypothesis a) the difference $\Delta\mu$ would have the following Taylor expansion

$$\Delta\mu = (\varrho - \varrho_c)\, \mu^{(1)}(T, \varrho_c) + \frac{1}{6} (\varrho - \varrho_c)^3\, \mu^{(3)}(T, \varrho_c) + \\ + \frac{1}{120} (\varrho - \varrho_c)^5\, \mu^{(5)}(T, \varrho_c) + \dots \tag{17a}$$

valid at any temperature T for densities $\varrho \sim \varrho_c$, where

$$\mu^{(1)}(T, \varrho_c) = 0 \text{ and } \mu^{(3)}(T, \varrho_c) = 0 \text{ if, and only if } T = T_c, \tag{17b}$$

by (5). In terms of Thom's catastrophe theory we can describe the characteristics of this expression as follows:

— the missing fourth order term in $(\varrho - \varrho_c)$ (i. e. $\frac{\partial^4 \mu}{\partial \varrho^4} = 0$ for all $T \geqq 0$ at $\varrho = \varrho_c$) together with conditions (17b) indicate that $\Delta\mu$, ϱ, T surfaces real gases are an example of so-called butterfly catstrophe;

- the absence of the square term in $(\varrho - \varrho_c)$ (i. e. $\partial^2\mu/\partial\varrho^2 = 0$ for all $T \geqq \geq 0$ at $\varrho = \varrho_c$) indicates that this is a special kind of butterfly catastrophe;
- the order parameter is the difference $(\varrho - \varrho_c)$; and
- there are three control parameters, the difference $\Delta\mu$, and two derivatives $\mu^{(1)}(T, \varrho_c)$ and $\mu^{(3)}(T, \varrho_c)$, which being functions of temperature only are not independent.

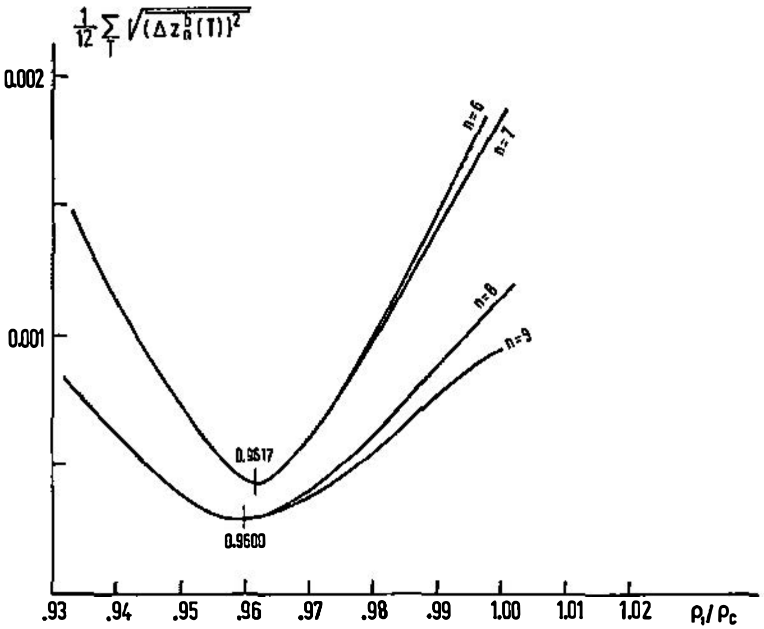

Fig. 6. The values of $\sqrt{\overline{(\Delta z_n^b(T))^2}}\,(\varrho_1)$ averaged over twelve isotherms of N_2 between −125 °C and +150 °C with $\varrho \in [0{,}2\,\varrho_c]$ for $n = 6, 7, 8, 9$ as functions of ϱ_1/ϱ_c. Vertical lines denote values of ϱ_1/ϱ_c which minimize $\frac{1}{12}\sum_T \sqrt{\overline{(\Delta z_n^b(T))^2}}\,(\varrho_1)$.

Were, however, the estimated incompatibility of hypothesis a) with experimental P, ϱ, T data not due only to fluctuations and experimental erros, and were it true that the estimated incompability (~ 0.05%) of P, ϱ, T data of the considered real gases with hypothesis b) was due only to fluctuations and experimental errors, and were $\partial^3\mu\,(\varrho = \varrho_c, T_c)/\partial\varrho^3 \neq 0$, then we would have the following Taylor expansion

$$\Delta\mu = (\varrho - \varrho_c)\,\mu^{(1)}(\varrho_c, T + \frac{1}{6}(\varrho - \varrho_c)^3\,\mu^{(3)}(\varrho_c, T) + \dots, \tag{18a}$$

where

$$\mu^{(1)}(T, \varrho_c) = 0 \text{ if, and only if } T = T_c. \tag{18b}$$

The peculiarities of this expansion would then imply in terms of Thom's catastrophe theory that

- $\Delta\mu$, ϱ, T surfaces exhibit explicity the so called cusp (Riemann-Hugoniot) catastrophe, as the square term in $(\varrho - \varrho_c)$ is missing at any temperature,
- the order parameter is the difference $(\varrho - \varrho_c)$, and
- there are two control parameters, the difference $\Delta\mu$ and (only) one function $\mu^{(1)}(T, \varrho_c)$ of temperature.

Hypotheses a) and b) being kinds of physical laws, a more detailed investigation of their compatibility with experimental data (i. e. of the »true« minimal value of $\max\limits_{T} \sqrt{(\Delta z_n(T))^2 (\varrho_{1\,min})}$ or of $\frac{1}{12} \sum\limits_{T} \sqrt{(\Delta z_n(T))^2 (\varrho_{1\,min})}$ is indicated, since it might result in more precise estimates of their actual accuracy. However, we will postpone further investigation for a substequent paper, because there are strong indications that (like Van der Waals' gases) experimentally determined P, ϱ, T surfaces also display approximately catastrophe-like behaviour around the critical density ϱ_c, and in the final analysis, the possibility of catastrophes of μ, ϱ, T and P, ϱ, T surfaces have to be examined concurrently.

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ANTISIMETRIJA EKSPERIMENTALNO DOLOČENIH KEMIČNIH POTENCIALOV REALNIH PLINOV IN THOMOVA TEORIJA KATASTROF

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Vsebina

Antisimetrija kemičnih potencialov $\mu(\varrho, T)$ realnih plinov okoli kritične gostote ϱ_c in Thomova teorija katastrof so nas spodbudili da smo preizkusili z eksperimentalnimi podatki naslednji dve hipotezi: a) $\partial^4\mu(\varrho_c, T)/\partial\varrho^4 = 0$ in $\partial^2\mu(\varrho_c, T)/\partial\varrho^2 = 0$ za vse T, in b) $\partial^2\mu(\varrho_c, T)/\partial\varrho^2 = 0$ za vse T. Dognali smo, da sta hipotezi a) in b) skladni z eksperimentalnimi podatki za Xe, CO_2, N_2, etilen in propen, če v povprečju spremenimo izmerjene podatke $P/RT\varrho$ za 0.2% oziroma 0.05%.