

NEW VAPOR PRESSURE MEASUREMENTS OF METHANOL OVER WIDE RANGE OF TEMPERATURES

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Abstract. Vapor pressure (VLE) of methanol was studied at temperatures $T = (274.15 \text{ K to } 468.67) \text{ K}$ using the two different static method installations. A glass cell was used below $T = 323.15 \text{ K}$. Experimental uncertainties for the glass cell are $\Delta T = \pm 0.01 \text{ K}$ and $\Delta P = \pm (10 \text{ to } 30) \text{ Pa}$ (MKS Baratron pressure sensor). A metal cell was used in the range $T = (323.15 \text{ to } 468.67) \text{ K}$. Experimental uncertainty of temperature measurements for the metal cell is $\Delta T = \pm 0.01 \text{ K}$. Pressure was measured with two different 35 X HTC Omega-Keller pressure transmitters. Reproducibility of the vapor pressure measurements is $\Delta P = \pm 1500 \text{ Pa}$ for the maximum pressure of 300000 Pa, $\Delta P = \pm 5000 \text{ Pa}$ for the maximum pressure of 1000000 Pa and $\Delta P = \pm 15000 \text{ Pa}$ for the maximum pressure of 3000000 Pa. A fundamental literature analysis of methanol has been done and experimental values were compared with the literature data. Measured values were fitted to the Antoine and Clausius-Clapeyron type equations.

Keywords: Methanol, vapor pressure, static method, Antoine equation, high temperature.

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1. Introduction

The price of traditional fuel is increasing every day. Alternative and renewable energy sources such as solar, wind energy, bio-diesel and biogas are becoming very important in many countries. Methanol has been proposed as an alternative to conventional gasoline and diesel fuels. Use of methanol as an alternative to conventional gasoline and diesel fuels dramatically increased last years. It can be successful used as a fuel in an internal combustion engine (Verhelst *et al.*, 2019).

Methanol is also commonly used as an inhibitor during the transportation of oil and gas to prevent hydrates from forming (Kvamme *et al.*, 2018; Bechtold *et al.*, 2007). The chemical potential of water is reduced by adding methanol to hydrocarbons. Because methanol and water have full solubility in all concentration ranges, a uniform distribution may be assumed. Methanol addition also increases octane number and lowers toxic hydrocarbon and carbon monoxide emissions. Most modern fuel systems can accommodate low-level methanol blends (up to 10%) without difficulty (Bechtold *et al.*, 2007), but addition of methanol increases the vapor pressure of the ternary (hydrocarbon+water+methanol) liquid mixture. Methanol has some high thermophysical properties: heat of vaporization, specific energy ratio, flame speed and molar expansion ratio. Such desirable attributes make it an excellent sparkignition engine fuel.

Industries like oil and gas production, refinement, and transport, require vast production of methanol. This production in turn requires an understanding of the physical

and chemical properties of methanol. Such properties were widely investigated during the last century, and some fundamental equations were developed.

We investigated also the various thermophysical properties of methanol:

- (p, ρ, T) properties at $T = (253.15 \text{ to } 468.65)$ K and at pressures up to $p = 200$ MPa,
- vapor pressure measurements P/Pa at $T = (274.15 \text{ to } 468.67)$ K,
- heat capacity measurements $c_{p0,s}/(\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1})$ at $T = (253.15 \text{ to } 468.67)$ K, ambient and saturated vapor pressures.

This work is the part of investigation of thermophysical properties of methanol and include the fundamental literature analysis of vapor pressure measurement, together with our new accuracy measurements using two different static method installations. Important publications on vapor pressure of methanol during the last 130 year has analysed below and the summary of these works presented in the Table 1.

Ramsay and Young, in 1887 used the Hoffmann apparatus for the determination of vapor pressure of methanol at $T = (258.54 \text{ to } 337.35)$ K. The boiling temperature at ambient pressure published in previous literatures were analysed. The pressure was measured using the millimeters of mercury.

Young, in 1910 measured the vapor pressure of methanol up to critical point at $T = (263.15 \text{ to } 513.15)$ K using two different apparatus. The dynamic method from Ramsay and Young, (1887) was used during the experiments up to vapor pressure of methanol around $P=66661$ Pa. A long-necked distillation-bulb with reflux condenser was employed for pressures $P=(66661 \text{ to } 101325)$ Pa. The glass thermometer placed in the vapor. The Andrew apparatus was use for the measurements at pressures higher than ambient pressure. The three different metal cells used during these measurements.

Mündel, in 1913 measured the vapor pressure of methanol at small temperatures at $T = (205.75 \text{ to } 228.75)$ K using a static method. The mercury manometer with an uncertainty in ± 0.0001 mm used during the measurements. Temperature was measured using a mercury glass thermomemeter. The uncertainty of temperature was to be $\Delta T = \pm 0.1$ K.

Schmidt, in 1926 measured the vapor pressure of methanol at $T = (273.15 \text{ to } 373.15)$ K. The uncertainty of temperature was as $\Delta T = \pm 0.01$ K and pressure $\Delta P/P = \pm 0.25\%$.

Dever et al., in 1955 measured the vapor pressure of commercial methanol at $T = (287.03 \text{ to } 307.26)$ K using a static method. Pressure was measure using a differential mercury manometer and pressure differences with a Gaertner cathetometer. The uncertainty of temperature was $\Delta T = \pm 0.01$ K. The over whole uncertainty in pressure measurement was $\Delta P/P = \pm 0.25\%$. The molar heat of vaporization ΔH_0 were calculated from the experimental vapor pressure values.

Kay and Donham, in 1955 investigated the VLE relations of binary mixtures of methanol and n-butanol, isobutanol-n-butanol and diethyl ether and n-butanol. During these measurements, also the vapor pressure of pure methanol was measured $T = (403.15 \text{ to } 512.58)$ K. The pressure was measured by confining a small, air-free sample over mercury in a glass tube, which was surrounded by a constant temperature bath. For controlling the sample pressure, the tube was fastened to a mercury filled compressor block. The uncertainties were in pressure $\Delta P = \pm 137$ Pa and in temperature $\Delta T = \pm 0.02$ K.

Miller, in 1964 measured the vapor pressure of methanol near melting point at temperatures $T = (175.04 \text{ to } 180.25)$ K using a Knudsen-gage, which has been cali-

brated using the known vapor pressures of ice, benzene and carbon tetrachloride at low temperatures. The vapor pressures of these three substances could be accurately extrapolate from the knowledge about the normal modes of vibration of these molecules at room temperature. Correction for thermal transpiration between sample and gage was made with an approximate form of the Weber equation. The vapor pressure was calculate using an Antoine equation. The heat of sublimation at absolute zero ΔH_0 was calculate from the vapor pressure.

Efremov, in 1966 studied the vapor pressure of methanol at $T = (313.15 \text{ to } 503.15) \text{ K}$ with an uncertainties in $\Delta T = \pm 0.1 \text{ K}$ using a capillary ampoule method.

Butcher and Medani, in 1968 measured the vapor pressure of pure methanol at temperatures $T = (373.15 \text{ to } 493.15) \text{ K}$. Additionally the corresponding activity coefficients of methanol and benzene were calculated. Integral heat of mixing and entropy change due to mixing as functions of liquid composition determined from the excess free energy of mixing functions.

Wolff and Höppel, in 1968 in their two publications measured the vapor pressure of pure methanol at temperatures $T = (308.15 \text{ to } 348.15) \text{ K}$ and $T = (293.15 \text{ to } 353.15) \text{ K}$ using a static method. Additionally the corresponding activity coefficients of methanol and benzene were calculated. Integral heat of mixing and entropy change due to mixing as functions of liquid composition determined from the excess free energy of mixing functions.

Broul et al., in 1969 measured the vapor-liquid equilibria for methanol, water, LiCl binary and ternary systems. The measured vapor pressure values at $T = (299.975 \text{ to } 337.695) \text{ K}$ were fitted to the Antoine equation.

Kojima and Kato, in 1969 measured the vapor pressure of methanol using the ebulliometer. The measurements were carried out at temperatures $T = (303.20 \text{ to } 442.67) \text{ K}$. The measurements were fitted to the Antoine equation. The activity coefficients of methanol and ethanol binary mixtures were calculated.

Tommila, in 1969 presented the vapor pressure values of methanol at $T = (283.15 \text{ to } 323.15) \text{ K}$ using a static method. Temperature was measured with an accuracy of $\Delta T = \pm 0.02 \text{ K}$. The pressure differences were measured with a cathetometer to the nearest hundredth of millimetre.

Zubarev and Bagdonas, in 1969 measured the vapor pressure of methanol at temperatures $T = (373.11 \text{ to } 508.53) \text{ K}$. The saturation line and critical parameters of methanol were analysed. The vapor pressure values were fitted to the polynomial equation. Heat of vaporisation were calculated from the experimental values.

Ambrose and Sprake, in 1970 measured the vapor pressure of methanol at temperatures $T = (288.049 \text{ to } 356.828) \text{ K}$ using a comparative ebulliometry method. In this method of two boilers connected by a pressure line. One boiler contains a reference fluid (water) and the other one contains the sample fluid. The boiling temperature of both fluids has to be measured. The measured values was correlated using an Antoine and Cragoe equations. They mentioned that water impurities could be responsible for uncertainties in the repeatability.

Boublik and Aim, in 1972 measured the saturated vapor pressure of methanol in the pressure range of $T = (274.869 \text{ to } 336.527) \text{ K}$ using the Swietoslowski standard ebulliometer. The ebulliometer was connected to a vacuum system with an accuracy of $\Delta P = \pm 6.7 \text{ Pa}$. Temperature was measured with an accuracy of $\Delta T = \pm 0.001 \text{ K}$. The measured data have been correlated using an Antoine equation. The heat of vaporization was calculated from the obtained values.

Chun and Davison, in 1972 measured the vapor pressure, excess free energies and excess enthalpies for the binary mixture of methanol and triethylamine over the whole concentration range and at temperatures $T = (283.15 \text{ to } 313.15) \text{ K}$ using a static method. The vapor pressure of pure methanol was performed at $P = (7506 \text{ to } 34937) \text{ Pa}$ interval. The temperature was controlled to within $\Delta T = \pm 0.03 \text{ K}$ by a thermistor-actuated proportional temperature controller. The overall uncertainty in pressure measurements was $\Delta P = \pm 13.3 \text{ Pa}$. The methanol samples were distilled from commercial products on a Stedman column at high reflux. The source and the mass fraction purity of the samples was not stated. The vapor composition and activity coefficients were calculated by the total pressure method in which the Gibbs-Duhem equation is integrated numerically with the total pressure liquid composition data. Excess Gibbs energy G^E and excess enthalpy H^E were determined using the experimental results.

Gibbard and Creek, in 1974 measured the vapor pressure of methanol at temperatures $T = (288.15 \text{ to } 337.15) \text{ K}$ in 5 K step. The obtained vapor pressure values was in $P = (9880 \text{ to } 101270) \text{ Pa}$ interval. From the measured data an empirical equation was derived. The static vapor-pressure apparatus contained of an oil thermostat, regulated at $\Delta T = \pm 0.001 \text{ K}$, for the vapor-pressure cell, and an air thermostat, regulated to $\Delta T = \pm 0.01 \text{ K}$, for the null manometer. The overall uncertainty in pressure and temperature measurement was $\Delta P = \pm 1 \text{ Pa}$ and $\Delta T = \pm 0.002 \text{ K}$.

Ambrose et al., in 1975 measured the vapor pressures of methanol for pressures higher than $P = 180000 \text{ Pa}$ and at temperatures $T = (353.46 \text{ to } 512.64) \text{ K}$ using a dynamic method with a upwards inserted thermometer. The pressures less than $P = 600000 \text{ Pa}$ were determined with an air-operated piston pressure balance made from a standard glass syringe. The results were fitted by equations in the form of Chebyshev polynomials. The enthalpy of evaporation was determined from the experimental values.

Apelblat and Kohler, in 1976 studied the vapor pressure of methanol in combination two various substances as binary mixture. The vapor pressure of methanol at temperatures $T = (298.18 \text{ to } 318.20) \text{ K}$ was determined by the isoteniscope method with some modifications. Excess Gibbs energy G^E was determined using the experimental results.

Aim and Ciprian, in 1980 used the standard Swietoslowski ebulliometer for measurements of the vapor pressure at temperatures $T = (299.178 \text{ to } 337.678) \text{ K}$. The overall uncertainty in temperature and pressure measurement was $\Delta T = \pm 0.005 \text{ K}$ and $\Delta P/P = \pm 0.02\%$. The measurements were carried out from the high pressure to downward. The received experimental values were fitted to the Antoine equation. The VLE of binary mixture, including the liquid and vapor composition were analysed for the every measured point and were fitted to the Wilson equation.

Machado and Streett, in 1983 calculated the vapor pressure of methanol using constructed equation of state. First they measured PVT properties of liquid methanol with a direct-weighing apparatus. These results were used for the 16 constant equation of state which determined the vapor pressure. The calculated values together with literature values for the vapor pressure of methanol were used afterwards for calculating the following thermodynamic values: specific volume, enthalpy of vaporization, isothermal compressibility, thermal expansion coefficient, and thermal pressure coefficient.

Olivares et al., in 1984 measured the vapor pressure of methanol at $T = (306.98 \text{ to } 331.32) \text{ K}$ using the ebulliometer. The uncertainty in temperature and pressure measurement was $\Delta T = \pm 0.04 \text{ K}$ and $\Delta P = \pm 1.3 \text{ Pa}$. The measured values was fitted to the Antoine equation.

Zawisza, in 1985 measured the dew and bubble points for methanol plus hexane over the whole concentration range at temperatures $T = (398.15 \text{ to } 48.15) \text{ K}$ and pressures $P = (200000 \text{ to } 4053000) \text{ Pa}$ using a static method. The sample was obtained from "Reanal" Hungary, were distilled and then used without further purification. For the vapor, the pressure and volume of the sample were measured at constant temperature between 0.1 MPa and the dew point. From this data the second virial coefficients and excess molar Gibbs energies have been calculated.

Goodwin, in 1987 summarized vapor pressure and orthobaric densities measurements of methanol previously published in 16 literature sources from 1887 to 1985 year, which used for correlation with an equation of state. The temperature range of this summary goes at $T = (288.09 \text{ to } 503.20) \text{ K}$ and pressures at $P = (9803 \text{ to } 6897400) \text{ Pa}$.

Oscarson *et al.*, in 1987 measured the vapor pressure of methanol with various binary systems. The temperature range where methanol was measured was $T = (331.90 \text{ to } 413.60) \text{ K}$ and pressures $P = (78000 \text{ to } 1096000) \text{ Pa}$. The measurements were made with a reflux bubble cap still installation.

Lydersen *et al.*, in 1990 measured the vapor pressure of methanol at high temperatures $T = (494.80 \text{ to } 511.75) \text{ K}$ using a volume change caused by condensation and vaporization. The obtained values were fitted to the simplified Clausius-Clapeyron equation in linear form.

Leu *et al.*, in 1992 measured the vapor pressure for the methanol-isobutane binary system at temperatures $T = (273.15 \text{ to } 423.15) \text{ K}$. From the phase composition data were calculated each component of the equilibrium at each temperature. They also measured the azeotropic pressures, the critical temperatures and corresponding critical pressure and associated compositions, but the expression relating azeotropic pressure and compositions were developed and the critical locus was constructed.

Esteve *et al.*, in 1995 measured the vapor pressure of methanol at the temperatures at $T = (293.15 \text{ to } 403.15) \text{ K}$ with 10 K intervals with the static method. The pressure measurements was carried out using a Ruska Model 6242 digital pressure gauge with an overall reproducibility in $\Delta P = \pm 100 \text{ Pa}$. The temperature of experiments was measured to better than $\Delta T = \pm 0.02 \text{ K}$. The Kuczynsky method was used to calculate the vapor and liquid compositions of the sample, also the pressure and temperature. It was observed that the system shows nearly ideal behavior at $T = 323.15 \text{ K}$. But at higher temperatures there are negative deviations and at lower temperatures positive deviations.

Mokbel *et al.*, in 1995 the vapor pressure of methanol at $T = (278.15 \text{ to } 323.15) \text{ K}$ using a static method. The uncertainty of the temperature was $\Delta T = \pm 0.02 \text{ K}$ and pressure $\Delta P/P = \pm(0.003 \text{ to } 0.02)\%$. The data were fitted to the Antoine equation.

Barton *et al.*, in 1996 measured the pressure of pure methanol at temperature $T=313.15 \text{ K}$ using a Bakers method and a Van Ness apparatus. The experimental uncertainty of pressure was $\Delta P = \pm 0.1 \text{ Pa}$ and of temperature $\Delta T = \pm 0.02 \text{ K}$. Vapor pressure values were reduced using Barker's method. The results of the data reduction procedure are a set of corrected liquid phase mole fractions for each pressure and values for the parameters appearing in the G^E model.

Blanco and Ortega, in 1996 studied the isobaric vapor-liquid equilibrium data at 141300 Pa for the binary systems methanol +n-pentane, +n-hexane using a small-capacity recirculating still installation. The uncertainties of pressure was in $\Delta P = \pm 0.5 \text{ mm Hg}$ and temperature in $\Delta T = \pm 0.01 \text{ K}$. The obtained vapor pressure values were fitted to the extended Antoine's equation. The vapour pressure values were used to calculate the activity coefficient values for the components in the liquid phase.

Table 1. Summary of the vapor pressure measurements for methanol

First author	Number of points	Method	Properties	Temperature, T/K	Pressure, P/Pa	Uncertainties		Purity	Company of purchase
						T/K	P		
Ramsay & Young, 1987	59	HA	P, T	258.54 to 337.35	1487 to 99085				LP
Young, 1910	31	DM, AA	P, T	263.15 to 511.15	2066 to 7954014				LP
Mündel, 1913	10	SM	P, T	205.75 to 228.75	13.6 to 131.46	±0.1	±0.67 Pa		LP
Schmidt, 1926	16		P, T	273.15 to 373.15	4253 to 328507	±0.1	±1.3 Pa		Merck AG
Fiock et al., 1931	15			273.15 to 403.15					
Dever et al., 1955	39	SM	P, T	287.03 to 307.26	9322 to 26790	±0.01	±0.25%	wat. <0.03%	Commercial
Kay & Donham, 1955	12	SM	P, ρ, T	403.15 to 512.58	8377743 to 8097488	±0.02	±138 Pa	High purity	Commercial
Mishchenko & Fedorov, 1961	7			278.15 to 323.15					
Miller, 1964	7	SM	P, T	175.04 to 180.25	0.17 to 0.41 Pa	±0.01	±3%	RGA	Commercial
Marinichev & Susarev, 1965	13			308 to 338					
Efremov, 1966	32	CAM	P, T	313.15 to 503.15	35464 to 6890100	±0.1		CP	Commercial
Zhilina & Mishchenko, 1967	9			283.15 to 323.15	7511 to 54209				
Butcher & Medani, 1968	7	SM	P, T	373.15 to 493.15	348198 to 5684928	±0.1	±0.125%	AG	Commercial
Wolff & Hoepfel, 1968a	7	SM	VLE	308.15 to 348.15	27958 to 150548	±0.01	±(40 to 54) Pa	99.96 mole %	Merck AG
Wolff & Hoepfel, 1968b	7	SM	VLE	293.15 to 353.15	12999 to 179959	±0.01	±(40 to 54) Pa	99.96 mole %	Merck AG
Broul et al., 1969	30	SM	VLE	299.975 to 337.695	18605 to 101241	±0.001	±0.06% (fitting)	TG	LP
Kojima & Kato, 1969	32	EB	VLE	303.20 to 442.67	21947 to 2176461				
Tommila et al., 1969	8	SM	P, T	288.15 to 323.15	9919 to 55342	±0.02	±1.3 Pa		Commercial
Zubarev & Bagdonas, 1969	28			373.11 to 508.53	352900 to 7677000				
Ambrose & Sprake, 1970	20	CE	P, T	288.049 to 356.828	9815 to 205653			99.9%	
Diaz Pena & Sotomayor, 1971	7	SM		293.15 to 338.15					
Boublik & Aim, 1972	16	SE	P, T	274.869 to 336.527	4524 to 96845	±0.001	±6.7 Pa	RGP	
Chun & Devison, 1972	4	SM	P, T	283.15 to 313.15	7506 to 34937	±0.03	±13.3 Pa		
Gibbard & Greek, 1974	21	SM	P, T	288.15 to 337.15	9.88 to 101.27	±0.002	±1 Pa	99.0 mole %	Fisher
Ambrose et al., 1975	24	DM	P, T	353.46 to 512.64	183.0 to 3310.8	±0.01	±10 Pa	99.99 mole %	
Apelblat & Kohler, 1976	8	IM	P, T, G ^E	298.18 to 318.20	17040 to 44655	±0.01	±0.02%	A.R.	BDH
Aim & Ciprian, 1980	17	SE	VLE, n _D	299.178 to 337.678	17900 to 101367	±0.005	±0.02%	A.R.	Lachema
Machado & Streett, 1983	18	EOS	P, V, T	298.15 to 473.15	16900 to 4013700	±0.05	±0.02%	99.98%	
Olivares et al., 1984	18	EB	VLE	306.98 to 331.32	26392 to 78340	±0.04	±1.3 Pa	99.97 mole %	Fisher
Zawisza, 1985	3	SM	P, V, T	398.15 to 448.15	735000 to 2420000			99.66%	Renanal
Oscarson et al., 1987	20	BCS	VLE	331.90 to 413.60	78240 to 1096000	±0.1	±1%	99.8%	MAR
Lydersen & Tsochev, 1990	8	VC	P, T, V	494.80 to 511.75	5960 to 7980	±0.05	5000 Pa	99.9%	Merck AG
Leu & Robinson, 1992	7		VLE	273.15 to 423.15	3900 to 1336000	±0.1	±0.15%	99.9 mole %	Fisher
Esteve et al., 1995	12	SM	VLE	293.15 to 403.15	13020 to 842200	±0.02	±100 Pa	>99.8%	Fluka
Mokbel et al., 1995	18	SM	VLE	239.15 to 313.15		±0.02	±(0.003 to 0.02)%	>99.8%	Prolabo

Barton et al., 1996	7	BM	VLE	313.15	35364 to 35437	±0.02	±0.1%	99.98%	<i>Aldrich</i>
Blanco & Ortega, 1996	47	EB	VLE	324.67 to 345.37	60410 to 137440	±0.01	±67 Pa	99.8%	<i>Fluka</i>
Coto et al., 1996	6	SM	VLE	298.15 to 338.15	16940 to 103040	±0.002	±0.08 %	>99.9%	<i>CER</i>
Toghiani et al., 1996	16	EB	VLE	300.22 to 348.80	18850 to 154640	±0.024	±26 Pa	99.9%	<i>Aldrich</i>
Aucejo et al., 1997	35	DRS	VLE	325.30 to 368.70	60830 to 309470	±0.1	±(10 to 100) Pa	99.85%	<i>Aldrich</i>
Garriga et al., 1997	10	SM	P, T, V, h	278.15 to 323.15	5488 to 55566	±0.01	±15 Pa	99.5%	
Antosik et al., 1999	11	SE	VLE	303.00 to 337.15	22022 to 101585	±0.01	±8 Pa	99.94%	<i>Aldrich</i>
Osada et al., 1999	14	MBVV	p_s, ρ, T	320.00 to 440.00	48.4 to 2049.7	±0.003	±0.001 Pa	99.8%	<i>WPCI</i>
Yokoyama & Uematsu, 2003	6	MBVV	p_s, ρ, T	320.00 to 420.00	48.4 to 1291.6	±0.001	±2500 Pa	99.8%	<i>WPCI</i>
Nasirzadeh et al., 2004	8	SM	P, T	298.15 to 333.15	16956 to 84612	±0.003	±0.01 %	99.8%	<i>Merck AG</i>
Bazaev et al., 2007	9	CVP	P, T, V	423.15 to 503.15	1399500 to 6905500	±0.015	±0.02 %	99.93 mole %	<i>Commercial</i>
<i>Safarov</i>	22	<i>SM</i>	P, T	<i>274.15 to 468.67</i>	<i>4252 to 3689392</i>	<i>±0.01</i>	<i>±(10 to 4000) Pa</i>	<i>99.9%</i>	<i>Merck AG</i>

HA, Hoffmann apparatus; LP, laboratory production; DM, dynamic method; AA, Andrew apparatus; SM, static method; wat., water amount; RGA, reagent grade anhydrous; CAM, capillary ampoule method; CP, chemical pure; AG, analar grade; VLE, vapor-liquid equilibria; TG, Technical grade; EB, Ebulliometer; CE, Comparative ebulliometry; SE, Swietoslowski ebulliometer; RGP, reagent grade purity; IM, isoteniscope method; A.R., analytical reagent; BDH, BDH Chemicals; EOS, equation of state; Calc., calculation; BCS, bubble cap still; MAR, Mallincrodt analytical reagent; VC, volume change method; BM, Barkers Method; SCRS, small-capacity recirculating still; CER, Carlo Erba Reagents; DRS, dynamic-recirculating still; MBVV, metal-bellows variable volumemeter; WPCI, Wako Pure Chemical Industries, CVP, constant volume piezometer; P , vapor pressure; T , temperature; ρ , density; G^E , Excess Gibbs Energy; n_D , refractive index; h , enthalpy; p_s , saturation pressure; p.w., present work.

The correlations for the Gibbs free energy function on the mole fraction of the liquid phase obtained using the equations of Margules, van Laar, Wilson, NRTL, UNIQUAC, Redlich-Kister and another function was carried out for the reduction of the equilibrium data.

Coto *et al.*, in 1996 studied the vapor – liquid equilibria of the methanol and *tert*-Butyl methyl Ether binary system. During this study, the vapor pressure of methanol at $T = (298.15 \text{ to } 338.15) \text{ K}$ using a Gibbs-Van Ness type static apparatus was measured. The temperature was controlled with an uncertainties $\Delta T = \pm 0.002 \text{ K}$ and pressure as $\Delta P/P = \pm 0.08 \%$. The excess Gibbs energy G^E , excess Enthalpy H^E and activity coefficients were calculated. The UNIQUAC model was used for the correlate VLE data. The physical interaction between associated complexes and unassociated molecules is described using the Sanches-Lacombe lattice-fluid theory.

Toghiani *et al.*, in 1996 measured the vapor pressure of methanol at $T = (300.22 \text{ to } 348.80) \text{ K}$ using an ebulliometer. Pressure was measured using a Ruska 6220 Sensor with an accuracy $\Delta P = \pm 26 \text{ Pa}$. Temperature was measured using a platine resistance thermometer with an accuracy of $\Delta T = \pm 0.024 \text{ K}$. The obtained vapor pressure values were fitted to the extended Antoine's equation.

Aucejo *et al.*, in 1997 studied the vapor pressure of methanol at $T = (325.30 \text{ to } 368.70) \text{ K}$ using a dynamic-recirculating still vessel. The equilibrium temperature was measured with a digital Fischer thermometer with an accuracy of $\Delta T = \pm 0.1 \text{ K}$. The installation is equipped with two pressure sensors: low-pressure zone with an accuracy of $\Delta P = \pm 10 \text{ Pa}$ and high-pressure range with an accuracy of $\Delta P = \pm 100 \text{ Pa}$. The measured vapor pressure values were fitted to the Antoine equation.

Garriga *et al.*, in 1997 used the static method for the measurements of vapor pressure of methanol in the temperature range $T = (278.15 \text{ to } 323.15 \text{ K})$ and pressures $P = (5488 \text{ to } 55566) \text{ Pa}$. The uncertainty of pressure was $\Delta P = \pm 15 \text{ Pa}$ and temperature $\Delta T = \pm 0.01 \text{ K}$. They also measured the volume and enthalpy for a better understanding of hydrogen bonding and associated systems in the liquid state.

Antosik *et al.*, in 1999 measured the vapor pressure of pure methanol at temperatures $T = (303.15 \text{ to } 337.15) \text{ K}$ application of the Swietoslowski's ebulliometer method, which was determined by using a Texas Instruments 144-01 precision pressure gauge with quartz Bourdon tube No. 8 type 2. The range of measured pressure was $P = (22022 \text{ to } 101585) \text{ Pa}$ with an uncertainty $\Delta P = \pm 10 \text{ Pa}$ and $\Delta T = \pm 0.01 \text{ K}$.

Osada *et al.*, in 1999 measured the vapor pressure of pure methanol and for its mixture with 50% H_2O at temperatures $T = (320 \text{ to } 420) \text{ K}$. Additionally pressure, density and temperatures measurements have been carried out for both samples in the same temperature range and pressures from the bubble point pressure up to $p = 200 \text{ MPa}$. Calculations for excess molar volumes have been done based on the measured data. The used apparatus was a metal-bellows variable volumometer. For the pressure measurements nitrogen was loaded into the a pressure vessel which contains the bellows with the sample methanol. The pressure was measured with different pressure gauges (Ruska: model 2465 and Futuba: model T and model TL2). The pressure vessel was immersed in a thermostatically-controlled bath. The uncertainties of the measurements were as follows: $\Delta T = \pm 0.003 \text{ K}$, $\Delta P = \pm 1 \cdot 10^{-3} P$ (in MPa) and $\Delta \rho = \pm 0.001 \text{ kg} \cdot \text{m}^{-3}$. The methanol sample was purified by fractional distillation, dried with molecular sieves for 36 h afterwards it was degassed.

Yokoyama and Uematsu, in 2003 measured the vapor pressure of the binary mixture of methanol and water over the whole concentration range and temperatures $T = (320 \text{ to } 420) \text{ K}$ with corresponding pressures at $P = (48400 \text{ to } 1291600) \text{ Pa}$. Additionally (p, ρ, T) measurements have been carried out. On the basis of these results excess molar volumes of the mixtures were calculated. The apparatus for the vapor pressure measurements was a metal-bellows variable volumometer. The pressure was measured with different pressure gauges (Ruska: model 2465 and Futuba: model T and model TL2). The pressure vessel was immersed in a thermostatically-controlled bath. The uncertainties of the measurements were: $\Delta T = \pm 0.001 \text{ K}$, $\Delta P = \pm 2 \cdot 10^{-3} P$ (in MPa) and $\Delta \rho = \pm 0.001 \text{ kg} \cdot \text{m}^{-3}$.

Nasirzadeh *et al.*, in 2004 measured the vapor pressure of LiBr and methanol solutions at temperatures $T = (298.15 \text{ to } 333.15) \text{ K}$ over the molality range $x = (0.0411 \text{ to } 6.8675)$ including the vapor pressure of pure methanol. The measuring apparatus with a static method was specially designed for precise vapor pressure measurements of pure fluids and of electrolyte solutions. The uncertainties were in temperature $\Delta T = \pm 0.003 \text{ K}$ and in pressure they were below $\Delta P/P = \pm 0.01\%$.

Bazaev *et al.*, in 2007 measured the vapor pressure of pure methanol for near-critical and supercritical regions with a constant-volume piezometer immersed in a precision air thermostat at temperatures $T = (423.15 \text{ to } 503.15) \text{ K}$ and the pressures $P = (1399500 \text{ to } 6905500) \text{ Pa}$. The uncertainty of the pressure is $\Delta P/P = \pm 0.02 \%$ and of the temperature $\Delta T = \pm 15 \text{ mK}$. The IUPAC equation for the correlation of experimental values were used and the wide range of literature comparison near critical area were carried out.

After the analysis of the available literature values we concluded that despite many measurements have been done and high accuracy was claimed, their results differ in the whole range (Table 1) in absolute and per cent deviations, so additional reliable measurements are necessary for arbitration.

2. Experimental

Materials. Ultra-pure methanol EMPSURE®, ACS, ISO, Reag. Ph Eur ($w=99.995\%$) was purchased from Merck KGaA, Germany (CAS No. 67-56-1, Art. Nr. 1.06.009.1000). methanol was thoroughly degassed in glass flask with special vacuum leak-proof valves (U.K.) before measurements.

Experimental Procedure. The vapor pressure measurements of methanol were measured using the two high-accuracy static experimental set ups (Safarov *et al.*, 2015a; Safarov *et al.*, 2015b). The glass cells are used for vapor pressures lower than ambient pressure at temperatures $T = (274.15 \text{ K to } 323.15) \text{ K}$ and the metal cell for vapor pressures at the temperatures $T = (323.15 \text{ K to } 468.67) \text{ K}$.

The glass cell method consists of absolute and differential parts (if the vapor pressure smaller than uncertainty of absolute cell – 30 Pa). The vapor pressure of methanol was every time higher than 30 Pa [uncertainty of measurements at $T = (274.15 \text{ to } 323.15) \text{ K}$]. In this case, the measurements in this temperature interval were carried out only using the absolute cell of installation. The glass cell static method consists of a bolted-top cell in a water bath kept at constant temperature ($\Delta T = \pm 0.01 \text{ K}$) using a thermostat. The vapor pressure is measured using a calibrated high accuracy sensor head [Type 615A connected to the signal conditioner Type 670A, MKS Baratron, USA] attached to the top of the cell. The experimental uncertainty of the pressure in the abso-

lute vapor pressure measurement using the glass cell is $\Delta P = \pm (10 \text{ to } 30) \text{ Pa}$. The temperature inside the cell is measured by a platinum resistance thermometer PT-100, connected to a signal conditioner Omega PT-104A, with an accuracy of $T = \pm 0.001 \text{ K}$. Experiments were carried out starting from low temperature ($T = 274.15 \text{ K}$) to high temperature $T = 323.15 \text{ K}$ at $\Delta T = 10 \text{ K}$ intervals using LabView computer programme control. Equilibration of the cells is a rapid process and a constant pressure in the stationary regime is reached within 15 minutes. Equilibrium pressure readings are performed in triplicate approximately (10 to 20) min. intervals.

The experiments to determine the vapor pressure of liquids at temperatures of $T = (323.15 \text{ to } 468.67) \text{ K}$ are performed in a metal cell using the static method. The internal volume of the measuring cell is appr. $V = 140 \text{ cm}^3$. The temperature of the measuring cell is controlled using a thermostat with an accuracy of $\Delta T = \pm 0.01 \text{ K}$. Temperatures are measured using two different platinum resistance thermometers, PT-100. The second platinum resistance thermometer, PT-100, transfers the measured temperature in the computer via an Omega PT-104A Channel RTD Input Data Acquisition Module (Omega Engineering, inc., USA) for the measuring of temperature, with an accuracy of $\Delta T = \pm 0.001 \text{ K}$. The vapor pressure is measured using three various Keller-Omega pressure transmitters: maximum pressure of 300000 Pa with uncertainty $\Delta P = \pm 1500 \text{ Pa}$, maximum pressure of 1000000 Pa with uncertainty $\Delta P = \pm 5000 \text{ Pa}$ and maximum pressure of 3000000 Pa with uncertainty $\Delta P = \pm 15000 \text{ Pa}$.

Before the experiments in both installations, the measuring cells were washed with water, methanol and acetone. All residual fluids were removed from the cells. This procedure requires approximately (2 to 3) h or more to reach the desired minimal pressure. At this point, all measuring cells are sufficiently dried and are ready for the experimentation. The measuring cell was dried to a minimal vacuum pressure of $P = (2 \text{ to } 10) \text{ Pa}$ in preparation for the experiments. Experiments were carried out starting from low temperature $T = 333.15 \text{ K}$ to high temperature $T = 468.67 \text{ K}$ at $\Delta T = 10 \text{ K}$ intervals using LabView computer programme control.

The vapor pressure of the water (Wagner & Prub, 2002) (APD in $\Delta P/P = \pm 0.106 \%$), ethanol (Talibov *et al.*, 2015; Schroeder *et al.*, 2014) (APD in $\Delta P/P = \pm 0.37 \%$), 1-propanol (Talibov *et al.*, 2016) (APD in $\Delta P/P = \pm 0.38 \%$), 1-butanol (Safarov *et al.*, 2015) (APD in $\Delta P/P = \pm 0.107 \%$), toluene (Lemmon & Span, 2006) (APD in $\Delta P/P = \pm 0.079 \%$) *etc.* were measured as reference substances for the testing of both setups.

3. Results and discussion

The measured experimental vapor pressures p of methanol at $T = (274.15 \text{ to } 468.67) \text{ K}$ are listed in Table 2. The temperature steps were $\Delta T = (5 \text{ to } 10) \text{ K}$.

The obtained experimental works were fitted to two different equations. Firstly, the experimental vapor pressure P results of methanol were fitted to the Antoine equation (Antoine, 1888a; Antoine, 1888b; Antoine, 1888c):

$$\ln(P/Pa) = A - B/\{(T/K) + C\}. \quad (1)$$

The evaluated constants A , B and C are tabulated in Table 3 together with the standard mean deviation as:

$$\Delta P/P = 100/n \cdot \sum_{i=1}^n [(P_{exp.} - P_{cal.})/P_{exp.}] \quad (2)$$

During the fitting of experimental values, we have seen, that Antoine equation fit the experimental values with not high accuracy. The uncertainty of fitting is $(P_{exp.} - P_{cal. Ant})/P_{exp.} = \pm 0.0601\%$. But, use of the extended version of Clausius–Clapeyron

equation (Clayperon, 1988b; Clausius, 1850) for fitting of the vapor pressure data for methanol reduced the fitting error:

$$\ln P = A + \frac{B}{T} + C \ln T + DT + ET^2, \quad (3)$$

where P is vapor pressure, Pa; T is the absolute temperature in K; A, B, C, D and E are the coefficients of equation. The uncertainty of fitting is decreased up to $(P_{exp.} - P_{cal.CC})/P_{exp.} = \pm 0.0467\%$. That is why the Clausius–Clapeyron type equation with four coefficients (A, B, C, D, E) was selected as the final fitting equation for the vapor pressure of methanol. The coefficients of equation (3) are tabulated in Table 4. The results of fitting also shown in the Figures 1 and 2.

Table 2. Experimental and calculated by Clausius-Clapeyron equation values of vapor pressure p of methanol

T/K	P_{exp}/Pa	$P_{cal.Ant}/Pa$	$(P_{exp} - P_{cal.Ant})/P_{exp}, \%$	$P_{cal.CC}/Pa$	$(P_{exp} - P_{cal.CC})/P_{exp}, \%$
274.15	4301	4297	0.0973	4301	-0.0030
278.15	5508	5505	0.0510	5507	0.0184
283.15	7419	7420	-0.0178	7418	0.0122
293.15	13019	13021	-0.0165	13008	0.0827
303.15	21899	21910	-0.0523	21885	0.0656
313.15	35470	35514	-0.1231	35476	-0.0156
323.15	55598	55664	-0.1189	55618	-0.0367
333.15	84584	84656	-0.0843	84612	-0.0325
343.15	125407	125290	0.0935	125261	0.1162
353.15	180995	180912	0.0460	180914	0.0445
363.15	255362	255441	-0.0308	255489	-0.0496
373.15	353752	353386	0.1036	353485	0.0754
383.15	480418	479851	0.1179	479996	0.0879
393.15	641127	640535	0.0923	640694	0.0676
403.15	841997	841710	0.0341	841821	0.0209
413.15	1090301	1090200	0.0092	1090161	0.0128
423.15	1393392	1393348	0.0032	1393009	0.0275
433.15	1758832	1758970	-0.0078	1758127	0.0401
443.15	2194795	2195316	-0.0237	2193704	0.0497
453.15	2709810	2711009	-0.0443	2708307	0.0555
463.15	3312704	3314998	-0.0693	3310823	0.0568
468.67	3686440	3689569	-0.0849	3684398	0.0554

Table 3. Antoine parameters A, B, C and standard deviations $\Delta P/P$

A	B	C	$(P_{exp} - P_{cal.Ant})/P_{exp}, \%$
23.4219	3598.78	-35.1280	± 0.0601

Table 4. Clausius - Clapeyron equation fitting parameters *A*, *B*, *C*, *D* and *E*

<i>A</i>	<i>B</i>	<i>C</i>
98.37059176	-6900.470789	-12.41546163
<i>D</i>	<i>E</i>	$(P_{exp}-P_{cal.CC})/P_{exp},\%$
0.01920181512	$-0.5337547876 \cdot 10^{-5}$	± 0.0467

From the comparison of presented results with those from literature show various deviations. The earliest vapor pressure values presented by Butler and Young on 1887 and some another old results have positive or negative deviations from presented results up to $\Delta P/P = \pm 0.37\%$ APD. Such situation mostly can be clearing at the results of purity of methanol, accuracy of installation, temperature or pressure measurements (mostly Hg Column). But, the values of Dever *et. al.* from 1955 has good deviation to presented results. At the results of comparison, it was clear, that presented values together with the values of Ambrose & Sprake, 1970; Boublik & Aim, 1972; Gibbard & Creek, 1974; Ambrose *et al.*, 1975; Aim & Ciprian, 1980; Esteve *et al.*, 1995; Toghiani *et al.*, 1996; Osada *et al.*, 1999; Yokoyama & Uematsu, 2003; Nasirzadeh *et al.*, 2004 can be using as reference values.

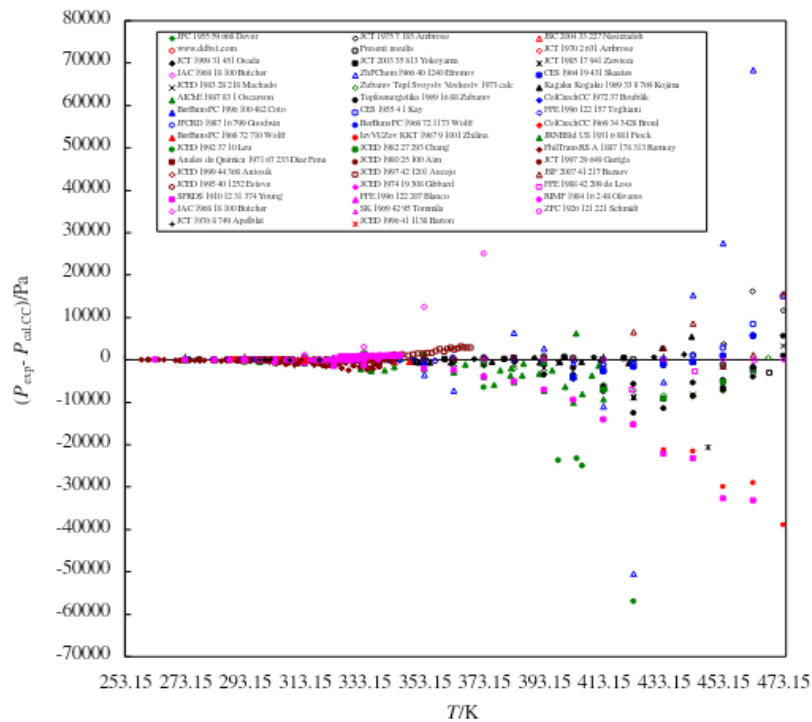


Figure 1. Plot of absolute deviation $(P_{exp}-P_{cal.CC})/Pa$ of experimental P_{exp} and literature P_{lit} . vapor pressure values of methanol *versus* temperatures T/K .

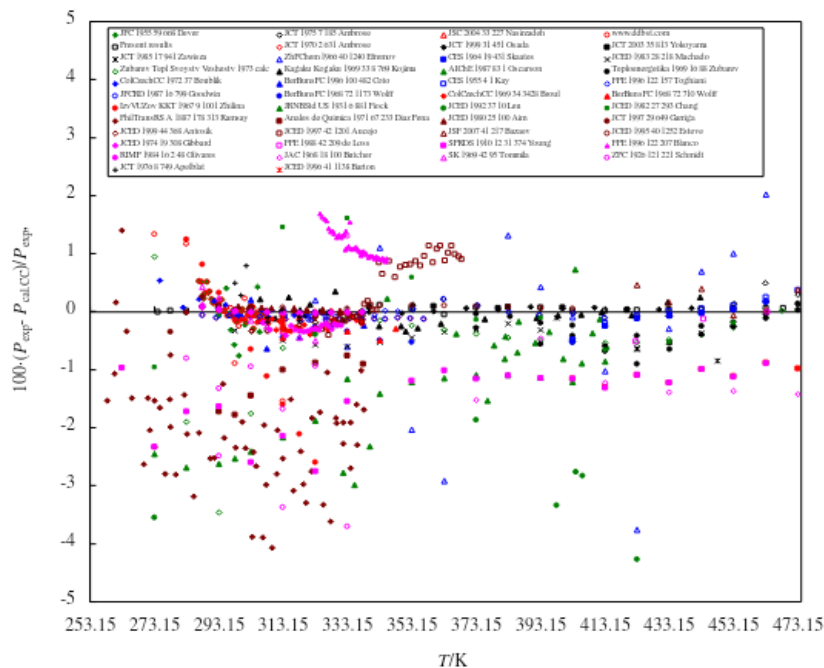


Figure 2. Plot of per cent deviation $(P_{exp}-P_{cal,CC})/P_{exp}$ of experimental P_{exp} , and literature P_{lit} , vapor pressure values of methanol *versus* temperatures T/K

The Clausius–Clapeyron type equation constructed in this work, was used for the analysing of literature values. The results of this analysis are shown in Table 5.

Table 5. Comparison of measured vapor pressure values of methanol with available literature values.

First author	T/K	AAD ^a / Pa	APD/ \pm , %	Deviation from present vapor pressure values
Ramsay & Young, 1987	327.95	2382	2.1601	<i>smaller</i>
Young, 1910	453.15	29993	1.4545	<i>smaller</i>
Schmidt, 1926	373.15	24978	3.0531	<i>mostly smaller</i>
Fiock et al., 1931	403.15	10044	1.7469	<i>mostly smaller</i>
Dever et al., 1955	299.49	137	0.2138	<i>close results, small deviation</i>
Kay & Donham, 1955	473.15	14891	0.1907	<i>close results, small deviation</i>
Efremov, 1966	463.15	68365	1.1643	<i>mostly smaller</i>
Zhilina & Mishchenko, 1967	323.15	1410	0.9474	<i>mostly smaller</i>
Butcher & Medani, 1968	373.15	56128	1.0525	<i>mostly smaller</i>
Wolff & Hoeppe, 1968a	343.15	618	0.2919	<i>mostly smaller</i>
Wolff & Hoeppe, 1968b	353.15	956	0.3104	<i>mostly smaller</i>
Broul et al., 1969	337.695	213	0.1999	<i>smaller, but small deviation</i>
Kojima & Kato, 1969	442.67	5400	0.1431	<i>positive and negative, but small deviation</i>
Tommila et al., 1969	323.15	276	0.2947	<i>positive and negative deviation</i>
Ambrose & Sprake, 1970	356.828	264	0.1216	<i>close results, small deviation</i>
Diaz Pena & Sotomayor, 1971	338.12	925	1.2113	<i>smaller</i>
Boublik & Aim, 1972	336.527	35	0.0994	<i>close results, small deviation</i>
Gibbard & Creek, 1974	323.149	19	0.0239	<i>close results, small deviation</i>
Ambrose et al., 1975	462.90	16184	0.1244	<i>positive and negative, but small deviation</i>

Apelblat & Kohler, 1976	301.75	163	0.2689	<i>positive and negative deviation</i>
Aim & Ciprian, 1980	316.54	25	0.0347	<i>close results, small deviation</i>
Chang et al., 1982	433.15	9127	0.6313	<i>positive deviation</i>
Machado & Streett, 1983	433.15	9127	0.4000	<i>negative deviation</i>
Olivares et al., 1984	328.24	208	0.2844	<i>negative deviation</i>
Zawisza, 1985	448.15	20579	0.5363	<i>negative deviation</i>
Oscarson et al., 1987	413.2	9334	0.9005	<i>negative deviation</i>
De Loos et al., 1988	422.82	7065	0.2139	<i>small deviation</i>
Leu & Robinson, 1992	423.15	57009	2.7148	<i>negative deviation</i>
Esteve et al., 1995	393.15	406	0.0754	<i>close results, small deviation</i>
Barton et al., 1996	313.15	112	0.2203	<i>negative deviation</i>
Blanco & Ortega, 1996	333.98	1370	1.1364	<i>positive deviation</i>
Coto et al., 1996	338.15	243	0.3058	<i>negative deviation</i>
Toghiani et al., 1996	341.53	72	0.0628	<i>close results, small deviation</i>
Aucejo et al., 1997	365.60	3174	0.5755	<i>mostly positive deviation</i>
Garriga et al., 1997	323.15	52	0.1085	<i>close results, small deviation</i>
Antosik et al., 1999	328.06	125	0.2490	<i>negative deviation</i>
Osada et al., 1999	440.00	1316	0.0654	<i>close results, small deviation</i>
Yokoyama & Uematsu, 2003	400.00	597	0.0671	<i>close results, small deviation</i>
Nasirzadeh et al., 2004	328.15	55	0.0515	<i>close results, small deviation</i>
Bazaev et al., 2007	473.15	15590	0.2991	<i>positive deviation</i>

^a AAD, Average absolute deviation; APD, Average percent deviation.

Also from these comparison, it is seen that the vapor pressure values for methanol at temperatures up to $T = 337.66$ K (normal boiling temperature at $P = 101325$ Pa obtained in this work by accuracy interpolation) have good agreement with most literature values. The large deviation between the experimental vapor pressure values of methanol and values obtained in the literature were obtained above normal boiling point of methanol. This fact have many reasons for the discussion. First, it is difficult to measure pressures much higher than ambient pressure with high accuracy, unlike MKS Baratron pressure sensors for lower pressures $\Delta P = \pm(10 \text{ to } 30)$ Pa. Modern pressure transmitters with mechanic membranes are used in such experiments. They have uncertainties 0.1%, sometimes 0.5 % of the maximal measured pressure. Our present results obtained with modern pressure transmitters and thermometers have the uncertainties up to $\Delta P = 0.1\%$. In this case, the uncertainties appr. $\Delta P = \pm 0.1\%$ of the measured vapor pressures above normal boiling point must be reasonable. It is impossible to obtain higher accuracy measurements in this region.

4. Conclusion

The vapor pressure of methanol at temperatures $T = (274.15 \text{ K to } 468.15) \text{ K}$ experimentally measured in two modern automatic installations based on the static method. The investigations in the wide range and high quality was carried out. The obtained experimental results were fitted by two different equations. The Clausius-Clapeyron type equation with four parameters showed the best fit. All available literature on vapor pressure of methanol was analyzed, and our experimental results were compared to that.

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