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Ideal-Gas and Saturation Properties of Methanol[1]

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Properties of the ideal gas have been considered in detail and new equations for the ideal-gas heat capacity enthalpy, and entropy are given which are valid from 100 to 1000 K. Saturation-curve data have been reviewed and an equation for the vapor pressure is given which covers the whole range from the triple point to the critical point. A tentative equation for the saturated liquid density is also given. The necessity for new experimental measurements is discussed.

KEY WORDS: critical point; density; heat capacity; ideal gas; methanol; saturation curve; triple point; vapor pressure.

1. INTRODUCTION

Methanol is becoming increasingly important in the chemical industry, as a prospective fuel and fuel additive [1]. In addition, it is of intrinsic interest as the first member of the homologous series of alkanols, and its physical properties, in conjunction with studies on other members, will help to characterize the properties of the series as a whole.

In view of this increasing interest, an analytic equation of state for fluid methanol is under development, and as a first step the ideal-gas and saturation properties are discussed here.

2. IDEAL-GAS PROPERTIES

The three recent tables of the ideal-gas properties, which are based on calculations from spectroscopic data, were published in 1955 by Ivash et al.

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[2], in 1977 by Chen et al. [3], and in 1979 by Glushko et al. [4]. The lowest temperature value in all three is 100 K, and the maximum ranges from 1000 K for Ivash et al. to 1500 K for Chen et al. and 6000 K for Glushko et al. The minimum temperature interval for any of the tables is 50 K. Values at closer intervals of temperature than are given in the published tables were kindly provided by Chao [5] using the molecular constants reported by Chen et al. The equations reported here are based mainly on these quantities.

2.1. Isobaric Heat Capacity

For methanol there are 6 translational and rotational and 12 internal degrees of freedom, 11 of which can be assigned to conventional vibrational modes. The twelfth is due to an internal rotation of the OH group about the C_3 symmetry axis of the methyl group and is characterized by a periodic potential energy function and a torsional oscillation frequency associated with motion in the wells of the potential energy curve. For temperatures above 100 K, the contribution to the isochoric heat capacity of the translational and rotational degrees of freedom is classical and equal to $3R$. The vibrational contributions, however, have significant temperature dependence and can be approximated by a group of simple harmonic oscillators of frequency ν_i each of which can be represented by the Einstein function $u_i^2 \exp(u_i)/[\exp(u_i)-1]^2$, where $u_i = hc\bar{\lambda}_i/kT$, h is the Planck constant, c the velocity of light, k the Boltzmann constant, T the absolute temperature, $\bar{\lambda}_i$ the wave number corresponding to the frequency ν_i, and R the gas constant. The vibrational wave numbers used by us were derived from values used by Chen et al. as selected by Shimanouchi [6].

Angus et al. [7], when representing C_p^{id} for propylene, obtained a satisfactory equation by using a single Einstein function, the wave number of which was an average of those making the largest contribution to the heat capacity in the temperature range of interest together with a few polynomial terms. A similar approach was tried for methanol by fitting the tabulated values of Chao over the range 100 to 1000 K, using an averaged wave number of 1046 cm^{-1}. The method of fitting used was that developed by Wagner [8], which statistically selects the most significant terms from an initial "bank." Although the resulting equation agreed well with the data used in the fit, an excessive number, 15, of polynomial terms were included, and when extrapolated to temperatures above 1000 K, the deviations between the data of Glushko et al. and the calculated values increased rapidly.

Therefore the bank of terms was changed to include only powers of $T \geqslant 0$ for the polynomial terms, thus ensuring finite values for C_p^{id}/R as

$T \rightarrow 0$. More Einstein terms were added, using wave numbers which were averages of those reported by Chen et al., and the internal rotation was also approximated with an Einstein term. In addition to 160 data points by Chao, 6 values from Glushko et al. were included for temperatures in the range 5500 to 6000 K. The final equation is

$$\frac{C_p^{id}}{R} = f_1 + \sum_{i=2}^{8} f_i \frac{u_i^2 \exp(u_i)}{[\exp(u_i) - 1]^2} \tag{1}$$

where $\tau = T_c/T$, $T_c = 512.64$ K, $u_i = g_i \tau$, and the f_i and g_i are given in Table I. The standard deviation of the experimental points from the curve was 2.59×10^{-4}.

Figure 1 shows the deviations between the literature values and those calculated from Eq. (1). The values of Chao, at all temperatures, lie well

Table I. (A) Coefficients and Wave Numbers Used in Eqs. (1)–(3), (B) Coefficients for Eq. (4), and (C) Coefficients for Eq. (6)

A

Coefficient	Coefficient value	Wave number (cm^{-1})	g_i
f_1	3.90086	—	—
f_2	10.9929	1470[a]	4.12575
f_3	18.3371	1165	3.26973
f_4	-16.3663	1345	3.77492
f_5	-6.22334	1046[a]	2.93574
f_6	2.80358	2935[a]	8.23747
f_7	1.07783	3681	10.3312
f_8	0.96967	190.0	0.53326

B

Coefficient	Value
a_1	2.09154
a_2	-8.99836
a_3	2.75404
a_4	-11.2352

C[b]

Coefficient	Value
b_1	2.34989
b_2	-1.59699
b_3	9.12479
b_4	-5.87973
b_5	-4.22760

[a] Average value.

[b] $\rho_c = 0.00884770$ mol · cm^{-3}.

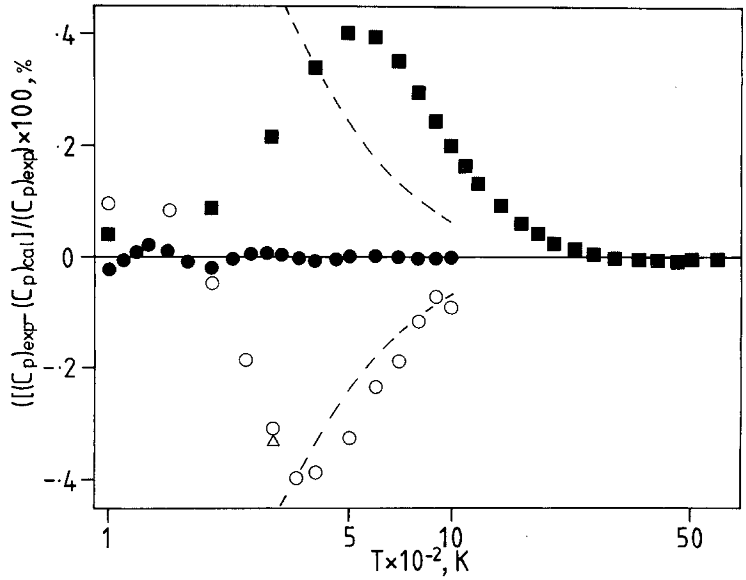

Fig. 1. Deviations of ideal-gas isobaric heat capacity data from Eq. (1). (●) Chao [5]; (■) Glushko et al. [4]; (○) Ivash et al. [2]; (△) Wagman et al. [9]; (– – –) error limits from Chen et al. [3].

within the uncertainty limits estimated by Chen et al. from considerations of available spectroscopic data.

The only polynomial term selected in the fitting procedure was the constant term, and therefore C_p^{id}/R will have finite values at all temperatures. The two limiting values of C_p^{id}/R, as $T \rightarrow 0$ and $T \rightarrow \infty$, which result from Eq. (1) are given by f_1 and $f_1 + \sum_{i=2}^{8} f_i$, respectively, and are 3.90 and 15.492. These compare well with the classical limits of 4.0 and 15.5.

Equation (1) represents the selected data to within ±0.02% for the temperature range 100–1000 K.

2.2. Entropy

If the reference state at which the entropy is taken to be zero is that of the ideal gas at 298.15 K and 0.1 MPa, then using Eq. (1), the entropy at any other temperature T and pressure P is given by

$$\frac{S^{id}}{R} = -f_1 \ln \tau + \sum_{i=2}^{8} f_i \left\{ \frac{u_i \exp(u_i)}{[\exp(u_i) - 1]} - \ln[\exp(u_i) - 1] \right\} + 0.941907 - \ln(P/0.1\ \mathrm{MPa}) \qquad (2)$$

The maximum deviation between the data of Chao and values from Eq. (2) is 0.014 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, which is well within the estimated uncertainties of Chen et al. ($\pm 0.45\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ at 200 K and $\pm 0.29\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ between 300 and 1000 K). The maximum deviation of the data of Ivash et al. is $-0.2\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ at 900 K, which is also within these uncertainties. The data of Glushko et al. show a systematic positive deviation from the equation over the range 100–1000 K where the maximum deviation is $+0.25\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ at 1000 K. Equation (2) represents the ideal-gas entropy to within $\pm 0.014\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ of the selected data.

2.3. Enthalpy

If the reference state at which the enthalpy is taken to be zero is that of the ideal gas at 298.15 K, then using Eq. (1), the enthalpy at any other temperature T is given by

$$\frac{H^{\mathrm{id}}}{RT} = \tau \left[\frac{f_1}{\tau} + \sum_{i=2}^{8} \frac{f_i g_i}{\exp(u_i) - 1} \right] - 1361.810\, \tau / T_{\mathrm{c}} \tag{3}$$

The maximum deviation between the data of Chao and values from Eq. (3) is $-1.8\ \mathrm{J \cdot mol^{-1}}$ at 920 and 340 K. This is well within the error limits quoted by Chen et al., which are $\pm 25\ \mathrm{J \cdot mol^{-1}}$ at 200 K, falling to zero in the reference state and rising again to $\pm 84\ \mathrm{J \cdot mol^{-1}}$ at 1000 K. At higher temperatures the deviations of Ivash et al. and of Glushko et al. are outside these limits. At 1000 K, the deviations of Ivash et al. are $-107\ \mathrm{J \cdot mol^{-1}}$ and those of Glushko et al. are $154\ \mathrm{J \cdot mol^{-1}}$, and at 3300 K those of Glushko et al. rise to $258\ \mathrm{J \cdot mol^{-1}}$. These large deviations are due to the systematic differences between the ideal heat capacities of the three sets of data (Fig. 1). Since the differences in $C_{\mathrm{p}}^{\mathrm{id}}$ between the data of Chao and those of Glushko et al. have the same sign, the deviations in enthalpy above 298.15 K between the two sets will increase with increasing temperature.

Equation (3) represents the enthalpy of the ideal gas to within $\pm 1.8\ \mathrm{J \cdot mol^{-1}}$ of the selected data.

3. CRITICAL POINT

Measurements of the critical properties are listed in Table II.

3.1. Critical Temperature

All the values were obtained by direct observation of the meniscus, except for that of Zubarev and Bagdonas, which was estimated from their *PVT* studies [18].

Table II. Measurements of the Critical Properties

Author(s)	Date [Ref. No.]	t_c (°C)	P_c (MPa)	ρ_c ($\mathrm{mol \cdot cm^{-3}}$)
Centnerszwer	1904 [10]	240.1	—	0.008392
Crismer	1904 [11]	240.5	—	—
Young	1909–1910 [12]	240.0	7.954	0.008495
Salzwedel	1930 [13]	240.0	10.0	0.0112
Fischer and Reichel	1943 [14]	240.6	—	—
Kay and Donham	1955 [15]	239.43	8.0972	0.00849
Skaates and Kay	1964 [16]	239.51	8.0938	—
Zubarev and Bagdonas	1969 [17]	239.5 ± 0.3	8.104 ± 0.4	0.00857

The value selected here is that of Kay and Donham [15], which when converted to the IPTS-68, gives $T_c = 512.64$ K. This value has been recommended by Ambrose [19].

3.2. Critical Pressure

With the exception of Zubarev and Bagdonas, the critical pressures were obtained by direct measurement in the apparatus used to determine T_c. The value selected here is that of Kay and Donham, 8.0972 MPa. A lower value of 8.092 MPa is recommended by Ambrose, which is closer to that of Skaates and Kay [16].

3.3. Critical Density

Salzwedel [13] determined ρ_c by extrapolating density values measured along the critical isobar to T_c, and Zubarev and Bagdonas made a graphical analysis of their data. The remaining results were obtained by applying the law of rectilinear diameter to saturation densities.

For consistency with saturated liquid densities we have selected the value of 0.0088477 $\mathrm{mol \cdot cm^{-3}}$; see Section 4.2.

4. SATURATION PROPERTIES

4.1. Vapor Pressure

Table III lists studies of the vapor pressure which cover the range from the triple point, 175.46 K, taken from Ref. 20 converted to IPTS-68, and

Table III. Measurements of the Vapor Pressure

Author(s)	Date	Temperature range (K)	Ref. No.
Mündel	1913	206–229	21
Colmant	1954	291–294	22
Dever et al.	1955	287–307	23
Kay and Donham	1955	403–512.64	15
Klyueva et al. (2 sets)	1960	285–323	24
Miller	1964	175–180	25
Hirata and Suda	1967	363–474	26
Zubarev and Bagdonas (3 sets)	1967	373–510	18
Ambrose and Sprake	1970	288–357	27
Gibbard and Creek (2 sets)	1974	288–338	28
Ambrose et al.	1975	353–463	29
Alm and Ciprian	1980	299–338	30

the critical point. The data were fitted by the procedure used for the ideal gas. All data points used were weighted according to the Gaussian error propagation formula using the reported experimental errors in P and T.

A preliminary fit to the data revealed systematic differences between the various sets. Ambrose and Sprake [27] used a comparative ebulliometric technique with water as the reference substance. This method is known to give results of high accuracy since the vapor pressure of water is well known; also, their reported water content was low (<0.01%), so their data were selected for the temperature range 288–357 K.

For higher temperatures the selection of data was much more difficult. Where the data of Ambrose et al. [29] overlap that of Ambrose and Sprake, there is a pressure difference of 0.15%; also, the Ambrose et al data end about 50 K below T_c. Where these overlap those of Kay and Donham [15], the maximum pressure difference is of the order of 0.4%. Also, the results of Kay and Donham have been published only as smoothed data, which causes difficulties in applying statistical weighting.

The three sets of Zubarev and Bagdonas were made using their *PVT* apparatus. Their measurements go to within about 3 K of T_c, but the reported water content is high (<0.27%) and the scatter is large. However, one of the sets of Zubarev and Bagdonas's data fitted smoothly with the selected Ambrose and Sprake data and resulted in a better fit than using those of Ambrose et al. and Kay and Donham. So the selected data were those of Ambrose and Sprake and Set 3 of Zubarev and Bagdonas. The resulting equation is

$$\ln(P/\mathrm{MPa}) = a_1 + \sum_{i=2}^{4} \frac{a_i}{\tau}(\tau - 1.0)^{i/2} \tag{4}$$

with the coefficients listed in Table I. The weighted standard deviation of the fitted data from the curve was 4.5. The value for the P_c predicted by this equation is 8.0973 MPa, which compares well with that measured by Kay and Donham. Deviations between the most reliable data and Eq. (4) are shown in Fig. 2 over the range 280 K–T_c. The equation extrapolates well below 280 K, where the curve falls midway between the experimental points.

Zubarev et al. [20] produced two equations for the vapor pressure, one valid from the triple point to 373 K and the other from 373 K to T_c. Deviations from their equations are shown in Fig. 2.

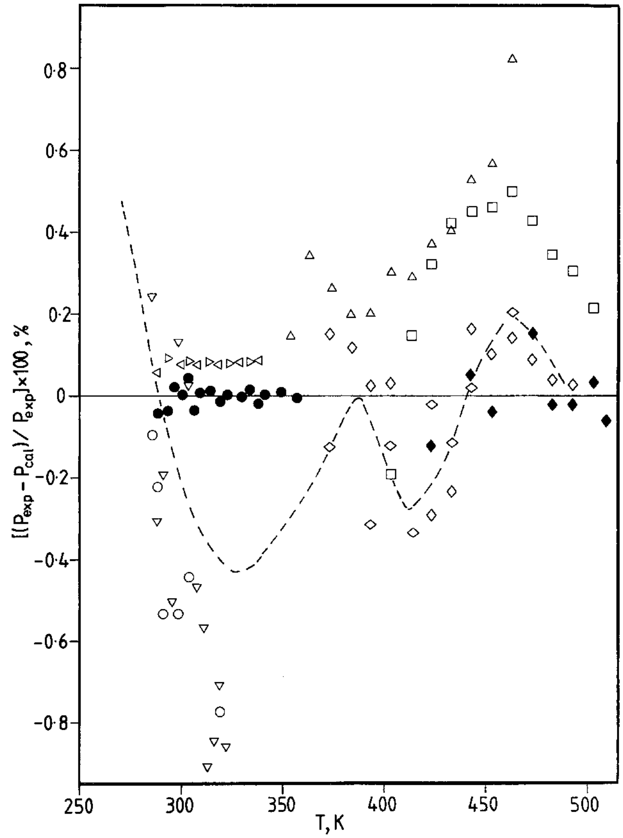

Fig. 2. Deviations of vapor pressure data from Eq. (4). (●) Ambrose and Sprake [27]; (△) Ambrose et al. [29]; (◁) Gibbard and Creek (set 1) [28]; (▷) Gibbard and Creek (set 2) [28]; (□) Kay and Donham [15]; (○) Klyueva et al. (set 1) [24]; (▽) Klyueva et al. (set 2) [24]; (◇) Zubarev and Bagdonas (set 1) [18]; (◇) Zubarev and Bagdonas (set 2) [18]; (◆) Zubarev and Bagdonas (set 3) [18]; (– – –) Zubarev et al. [20].

For such a well-studied fluid as methanol, the systematic discrepancies between the data sets is surprising and cause for concern. It is essential that only samples of the highest purity are used in the determination of accurate data. Pure methanol is very difficult to prepare. It is very hygroscopic and, once dried, must be kept away from moist air. Drying procedures which have been used include treatment with sodium [15], magnesium ribbon [30], calcium hydride [25], zeolites [27], and calcium sulfate [31], followed by fractional distillation. Additionally, above 473 K decomposition may occur [32] and may affect results near the critical point.

Vapor pressures calculated from Eq. (4) should be accurate to within $\pm 8\%$ ($\pm 1.5 \times 10^{-8}$ MPa) at the triple point, falling to $\pm 0.1\%$ (1.9×10^{-5} MPa) at 300 K. Between 300 K and the normal boiling point (337.65 K), the accuracy should be within $\sim 0.1\%$. Thereafter Eq. (4) reproduces the data used in the fit to within 0.15% at 473K (6.15×10^{-3} MPa) but the scatter of the available data between the normal boiling and the critical points precludes the recommendation of any firm limits.

4.2. Saturated Liquid Densities

Saturated liquid densities have been measured by Kay and Donham [15] in 1955 for the temperature range 403–513 K and by Hales and Ellender [31] in 1976 for the temperature range 293 to 440 K. A preliminary fit showed differences between the two sets which were greater than the sum of the error limits given by the authors. Since the data of Kay and Donham were smoothed values and had not been used for the vapor pressure curve, the data of Hales and Ellender were chosen.

In order to find a value for ρ_c consistent with the data, the following iterative procedure was used.

(a) The data were fitted using a value for ρ_c.

(b) Saturated vapor densities, ρ_V, were calculated from the equation

$$\rho_V = 1/[1/\rho_L + (\Delta H_{vap}/T)(dP/dT)^{-1}] \qquad (5)$$

where ΔH_{vap}, the enthalpies of vaporization, were taken from Refs. 33–39 and dP/dT was calculated from Eq. (4).

(c) Corresponding ρ_L and ρ_V values were combined according to the law of rectilinear diameters.

(d) A new value for ρ_c was calculated from step c at T_c. Steps a–d were repeated until consistent values of ρ_c were found.

The final value of ρ_c, 0.0088477 $\mathrm{mol \cdot cm^{-3}}$, was higher than that measured by Kay and Donham. The final equation is

$$\ln(\rho_L/\rho_c) = b_1(\tau - 1)^{1/3} + b_2(\tau - 1)^{1/2} + b_3(\tau - 1) + b_4(\tau - 1)^{7/6} + b_5 \ln \tau \quad (6)$$

with the coefficients b_i listed in Table I. The weighted standard deviation, of the data used in the fit, from the curve was 0.28.

Equation (6) represents the data of Hales and Ellender [31] within their experimental error. The maximum deviation of the data of Kay and Donham is −1.5%, and the tabulated values of Zubarev et al. vary from +0.1% to −1.5% near T_c. Values for the saturated liquid density calculated from Eq. (6) should be regarded as upper limits only, and new measurements along the whole of the saturation curve are required to clarify the situation.

4.3. Saturated Vapor Densities

The only set of saturated vapour density data is that of Kay and Donham [15] for the temperature range 453–513 K. Since vapor density measurements may be subject to large adsorption errors [40] and because of the discrepancies in the saturated liquid density data, their values have not been fitted, but only compared with values determined from Eqs. (4)–(6) using enthalpy of vaporization data in Refs. 33–39, and the values given by Zubarev et al. [20].

Values calculated from enthalpy data agree reasonably well with the measurements of Kay and Donham in the region of overlap, but values calculated from the law of rectilinear diameters are in poor agreement. Values from the tables of Zubarev et al. lie between the two. For the temperature range covered here, saturated vapor densities calculated from enthalpy data are relatively insensitive to errors in the saturated liquid densities but are dependent on the accuracy of the vapor pressure equation and the enthalpies. The accuracy of the enthalpy of vaporization data is ±0.2% at room temperature, rising to about ±0.9% at 477 K [35, 39]. The total accuracy probably lies outside that achievable with the best *PVT* apparatus, but for methanol, especially at low temperatures, adsorption problems are severe [40, 41] and these values may be preferable.

5. CONCLUSIONS

The work described here has revealed gaps and inconsistencies in the available data for methanol and demonstrated the need for more experimental measurements. In particular, vapor pressure measurements between the normal boiling and the critical points, together with the critical temperature, and saturated liquid densities and enthalpies of vaporization over the whole of the saturation curve are needed.

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