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Isochoric (p, v, T) Measurements on CO_2 and ($0.98\,CO_2 + 0.02\,CH_4$) from 225 to 400 K and Pressures to 35 MPa

J. W. Magee[1] **and J. F. Ely**[1]

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Comprehensive isochoric (p, v, T) measurements have been obtained for ($0.98\,CO_2 + 0.02\,CH_4$) at densities from 1 to 26 mol · dm^{-3}. Supplemental isochoric (p, v, T) measurements have been obtained for high-purity CO_2 at densities from 12 to 24 mol · dm^{-3}. Measurements of $p(T)$ cover a broad range of temperature, 225 to 400 K, at pressures to 35 MPa. Comparisons have been made with independent sources and with a predictive method based on corresponding states.

KEY WORDS: carbon dioxide; density; high pressure; isochoric; mixtures.

1. INTRODUCTION

The behavior of the (p, v, T) surface constitutes one of the most important and fundamental properties of pure fluids and their mixtures. Among the chief uses of the (p, v, T) surface is its incorporation into data bases for development and testing of predictive models for thermodynamic properties of fluid mixtures. Comprehensive (p, v, T) measurements on broad classes of mixtures are needed for this purpose.

During the past 10 years, great interest has developed in the properties of pure CO_2 and CO_2-rich mixtures. This interest has evolved from several sources, notably enhanced oil recovery using CO_2 and related CO_2 pipeline and gas processing technologies. The most common diluent found in CO_2 pipelines is CH_4, typically 0.02 mole fraction or less. Hence, $0.98\,CO_2 + 0.02\,CH_4$ represents an analogue mixture often found in CO_2 pipelines. In addition, many potential applications for using CO_2 as a

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[1] Thermophysics Division, National Bureau of Standards, Boulder, Colorado 80303, U.S.A.

solvent in supercritical fluid extraction exist. As a result, predictive models founded upon accurate measurements are needed in design and process operation calculations.

2. EXPERIMENTAL

The apparatus used in this work has a long history including studies of pure fluids and mixtures [1–7]. Just before this study, the apparatus was modified extensively to allow automated data acquisition and control and to raise the upper limit of temperature from 330 to 450 K. The experimental method has been called the isochoric (constant volume) method and is used without deviation from widely known procedure. In this method, a sample of fixed mass is confined in a container of nearly fixed volume. The volume of the container (Fig. 1) is accurately known as a function of pressure and temperature. The temperature is changed in increments, and pressure is measured at each temperature until the upper limit of temperature or pressure (35 MPa) is obtained. When the upper limit of the run has been reached, the sample is cryopumped into a weighing cylinder which is immersed in boiling liquid nitrogen. This gravimetric technique gives the sample mass from the difference of precise weighings before and after the sample is trapped in the weighing cylinder.

The density of the sample fluid is determined from a knowledge of the sample mass and the volume of the cell at each pressure and temperature on the run. Although the volume is only approximately constant, we refer to the run as an isochore, as is common practice. Pressures are measured by reading the average period of vibration, over a given time interval, of an oscillating quartz crystal transducer which is connected to the sample container (cell) through a fine-diameter (0.03-cm-OD) capillary, seen in Fig. 2. The transducer, thermostated at 333.15 ± 0.05 K, has been calibrated versus an oil-lubricated piston gauge, accurate to 0.01 %. The calibration was performed before and after completion of this study. As Fig. 3 shows,

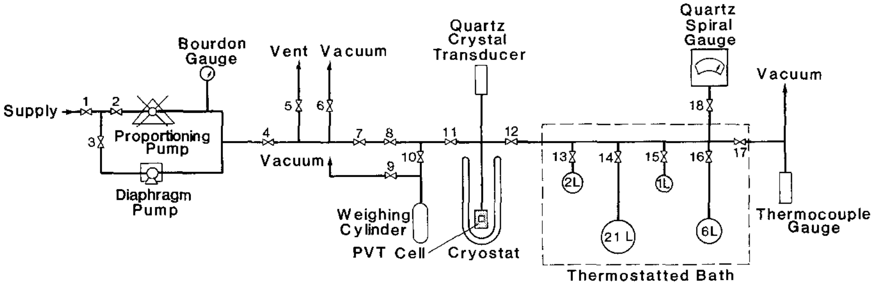

Fig. 1. Schematic diagram of isochoric (p, v, T) apparatus.

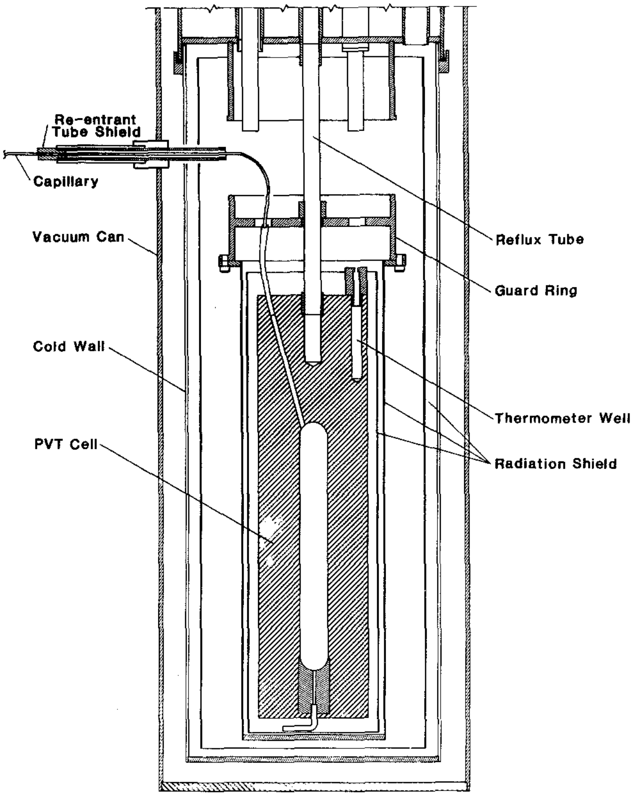

Fig. 2. Details of (*p*, *v*, *T*) cell and cryostat.

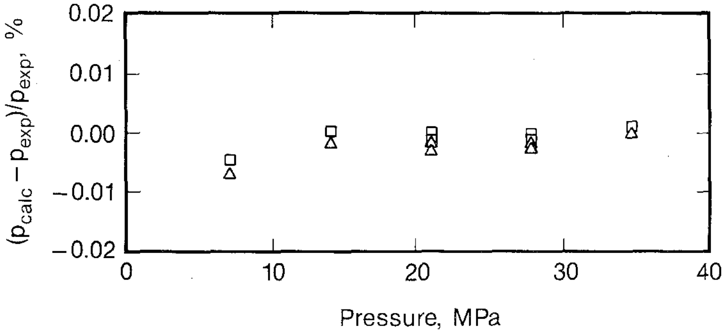

Fig. 3. Deviations of two sets of calibration data for quartz pressure transducer from piston gauge pressures: 7–1–87 □; 5–2–86 △.

our transducer is extremely table over this 14-month span, since it exhibits deviations from the original calibration of less than 0.0003 %. A regression routine has been used to fit the pressure (p)/period(τ) data to the relation,

$$p = C\{1 - (\tau_0/\tau)^2 - D[1 - (\tau_0/\tau)^2]^2\}$$

where τ_0 is the average period at zero pressure and C and D are coefficients of the model. The root mean square (RMS) deviation of the pressures was found to be 0.0052 % following this study, while the former calibration coefficients yielded a 0.0054 % RMS deviation from the most recent calibration data.

Temperatures are measured with a platinum resistance thermometer (PRT) circuit which incorporates a 25-Ω PRT calibrated on the IPTS-68 by the NBS Temperature Section, a precision current source, a 10-Ω standard resistor calibrated by the NBS Electricity Division, low thermal emf solder connections, ultralow thermal emf relays, and a 6.5-digit nanovoltmeter. The current source powers the thermometry circuit with 2 mA and is equipped with relays capable of reversing the direction of current in the circuit. Thus, we are able to average forward and reverse readings of potential, completely eliminating errors associated with any spurious emf's.

Readings of our transducer's period of oscillation and readings of potentials in the thermometry circuit are communicated to the host microcomputer by an IEEE-488 standard interface. In turn, relays and power supplies are controlled with digital and analog signals, respectively. A FORTRAN program is responsible for automated data acquisition, control, and data processing. It controls relay closures, current directions, instrument readings, and heater power. It employs a proportional plus integral control scheme for the apparatus heaters. In addition, the program scans a range of target temperatures, recording data when equilibrium conditions are detected as shown by temperature and pressure derivatives with time falling below threshold values. Another useful feature of the program allows monitoring and complete control to be shifted to any remote location equipped with a modem and a microcomputer.

The carbon dioxide and methane used in this study are research-grade gases. The minimum purities specified by the gas suppliers are 0.9999 CO_2 and 0.9997 CH_4. Chromatographic analyses of our gases revealed purities of 0.999946 CO_2 and 0.99999 CH_4.

The mixture was prepared gravimetrically in a thoroughly cleaned and dried aluminum cylinder. Weighings were performed with a double-pan 25-kg balance that had a certified standard deviation of 0.51 mg. The resulting compositions and estimated uncertainties of the mole fractions are

0.97954 ± 0.00005 CO_2 (0.00004 due to impurities) and 0.02046 ± 0.00003 CH_4. A total of 40 mol was prepared in a cylinder of approximately 11 dm^3. The final mixture pressure at ambient temperature was approximately 5 MPa, which is less than the vapor pressure of pure CO_2 (6 MPa) at ambient temperature. The storage pressure is also less than the dew-point pressure of our mixture. Thus, the mixture is stored at ambient temperature as a single-phase vapor.

When charging a mixture sample to the cell, precautionary steps were taken to avoid phase separation of the sample whose critical temperature is above ambient. Thus, our 11-dm^3 cylinder was heated nearly to 340 K on a hot plate, while other volumes in the gas charging system were warmed with heat lamps. With the cell heated to 320 K, the entire system was evacuated, then repeatedly purged with hot sample gas. A diaphragm compressor was used to boost the gas pressure in the cell to a target pressure estimated by a predictive computer program developed by Ely [8] and based on corresponding states.

Demixing of a sample during a run was found to be a neglible effect. For this test, pressure measurements at 320 K were carefully repeated at these times: (1) when the sample was charged, (2) during the normal course of a run, and (3) just before the sample was discharged. For each run, agreement of the pressures was better than 0.001 %. These tests also served to prove the absence of leaks.

3. RESULTS

Owing to the considerable modifications to the apparatus before this work, all volume elements were recalibrated. We used hydrogen expansions from a glass bulb whose volume is known to ±0.01 % by careful weighings with pure water. At 300 K, the cell volume was determined to be $28.787 \pm 0.014\ cm^3$. Separate hydrogen exapansions were used to measure the noxious volumes (transducer, 0.074 cm^3; manifold, 0.139 cm^3) maintained at 333.15 K. Corrections for the mass of vapor resident in these noxious volumes were small in every case. The first measurements were made on 0.999946 CO_2 in order to test the performance of the apparatus. CO_2 was selected because of its high purity, its suitability for cryopumping into a weighing vessel, and the availability of accurate (p, v, T) data from this laboratory and others for comparison.

Three CO_2 isochores were measured for this purpose. Table I gives the temperature (K), pressure (MPa), and density ($mol \cdot dm^{-3}$) for CO_2 at nominal densities 12, 17, and 24 $mol \cdot dm^{-3}$. The temperature range is 250 to 330 K, while pressures extend to 27 MPa. Sample masses ranged from 15 to 30 g and are accurate to within 0.002 g. Our temperatures are

Table I. Experimental (p, v, T) for CO_2

T (K)	P (MPa)	ρ_{exp} ($mol \cdot dm^{-3}$)	ρ_{calc} ($mol \cdot dm^{-3}$)[a]	Dev. (%)[b]
310.000	8.509	11.812	11.795	0.145
320.000	10.514	11.791	11.816	0.217
330.000	12.546	11.764	11.788	−0.200
300.000	8.243	17.301	17.298	0.020
310.000	12.423	17.257	17.263	−0.035
320.000	16.656	17.222	17.226	−0.024
330.000	20.945	27.202	17.202	−0.014
250.000	5.817	24.148	24.122	0.109
260.000	16.265	24.062	24.034	0.116
270.000	27.056	24.023	23.993	0.124

[a] Density calculated from equation of state [9].
[b] Deviation = 100 $(\rho_{exp} - \rho_{calc})/\rho_{exp}$.

accurate within ±0.030 K and are reproducible to ±0.001 K. Pressures are accurate to ±0.01 % and are reproducible to ±0.001 %. Overall, densities are accurate to better than 0.1 %, with the mass and volume measurements contributing the most to the uncertainty.

Comparisons of these data with others is facilitated by a recent equation of state [9] which incorporates a functional form designed to improve predictability in the critical region. Figures 4 and 5 show deviations of the experimental densities from the equation of state [9]

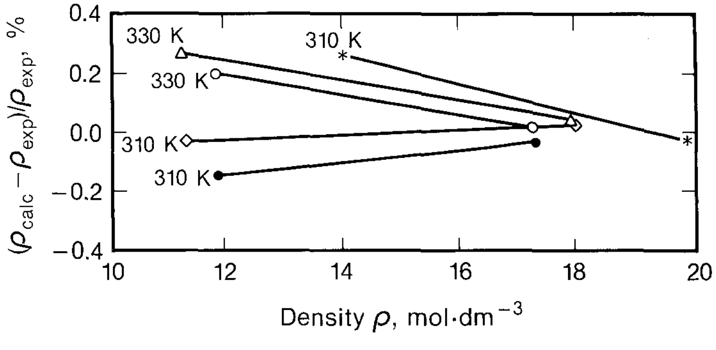

Fig. 4. Deviations of carbon dioxide densities calculated with equation of state [9] from this work and from independent sources of data. At 310 K: ● this work; ◇ Haynes et al. [10]; * Holste et al. [11]. At 330 K: ○ this work; △ Haynes et al. [10].

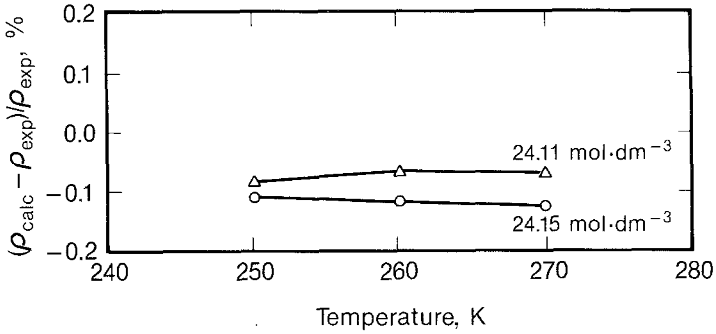

Fig. 5. Deviations of carbon dioxide densities calculated with equation of state [9] from this work ○ and from Haynes et al. [10] △.

along with similar deviations for the data of Haynes et al. [10] and Holste et al. [11]. Note the close agreement among all three sources of data. A spread of 0.1 % is typical and is within the uncertainty of the data. As expected, at 310 K near the critical density, a spread of 0.3 % is shown, which reflects how a small discrepancy in pressure scales between laboratories is amplified for densities in the critial region.

With the performance of our apparatus verified, measurements were carried out on the $0.98\ CO_2 + 0.02\ CH_4$ mixture. Table II gives the tem-

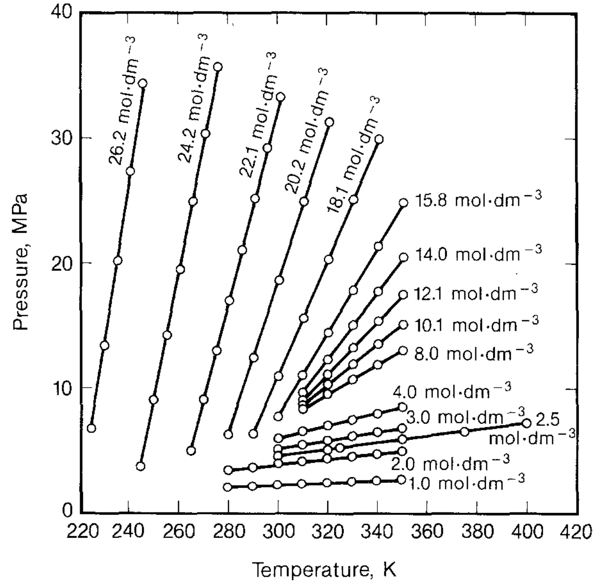

Fig. 6. Pressure and temperature ranges of this work's experimental (p, v, T) results for $(0.98\ CO_2 + 0.02\ CH_4)$.

Table II. Experimental (p, v, T) for $0.98\ CO_2 + 0.02\ CH_4$

T (K)	P (MPa)	ρ_{exp} $(mol \cdot dm^{-3})$	ρ_{calc} $(mol \cdot dm^{-3})^a$	Dev. $(\%)^b$
280.000	2.063	1.031	1.027	0.332
290.000	2.163	1.030	1.027	0.296
300.000	2.261	1.029	1.026	0.293
310.000	2.358	1.028	1.026	0.279
320.000	2.454	1.028	1.025	0.251
330.000	2.549	1.027	1.024	0.229
340.000	2.644	1.026	1.024	0.204
350.000	2.738	1.025	1.023	0.181
280.000	3.473	2.040	2.014	1.275
290.000	3.702	2.038	2.016	1.078
300.000	3.932	2.036	2.022	0.715
310.000	4.158	2.034	2.027	0.351
320.000	4.371	2.032	2.026	0.326
330.000	4.580	2.031	2.024	0.303
340.000	4.787	2.029	2.024	0.246
350.000	4.992	2.027	2.023	0.189
300.000	4.577	2.509	2.503	0.214
320.000	5.130	2.504	2.498	0.257
325.000	5.269	2.503	2.499	0.138
350.000	5.933	2.497	2.496	0.035
375.000	6.576	2.487	2.491	−0.174
400.000	7.205	2.480	2.487	−0.274
300.000	5.137	3.018	2.995	0.756
310.000	5.494	3.015	2.996	0.630
320.000	5.843	3.012	2.997	0.505
330.000	6.186	3.009	2.998	0.368
340.000	6.521	3.002	2.996	0.203
350.000	6.851	2.999	2.995	0.124
300.000	6.016	4.043	4.012	0.759
310.000	6.541	4.035	4.017	0.452
320.000	7.046	4.031	4.014	0.411
330.000	7.541	4.026	4.014	0.314
340.000	8.024	4.022	4.011	0.259
350.000	8.497	4.017	4.008	0.222
310.000	8.353	7.964	7.939	0.315
320.000	9.568	7.953	7.920	0.412
330.000	10.756	7.940	7.902	0.468
340.000	11.924	7.925	7.890	0.439
350.000	13.075	7.910	7.880	0.385
310.000	8.709	10.070	9.955	1.152
320.000	10.331	10.054	9.988	0.656
330.000	11.945	10.035	9.991	0.431
340.000	13.551	10.015	9.986	0.296
350.000	15.148	10.000	9.977	0.228

[a] Density calculated from corresponding states [8].

[b] Deviation = 100 $(\rho_{exp} - \rho_{calc})/\rho_{exp}$.

Table II. *(Continued)*

T (K)	P (MPa)	ρ_{exp} $(\mathrm{mol \cdot dm^{-3}})$	ρ_{calc} $(\mathrm{mol \cdot dm^{-3}})^a$	Dev. (%)^b
310.000	9.081	12.134	12.016	0.971
320.000	11.172	12.112	12.068	0.362
330.000	13.292	12.087	12.082	0.036
340.000	15.422	12.066	12.076	−0.082
350.000	17.558	12.050	12.065	−0.125
310.000	9.704	13.990	13.968	0.154
320.000	12.371	13.960	13.970	−0.071
330.000	15.080	13.933	13.956	−0.169
340.000	17.818	13.913	13.939	−0.188
350.000	20.569	13.897	13.919	−0.159
300.000	7.751	15.764	15.809	−0.288
310.000	11.070	15.733	15.753	−0.125
320.000	14.475	15.697	15.724	−0.172
330.000	17.928	15.672	15.697	−0.155
340.000	21.414	15.654	15.672	−0.120
350.000	24.912	15.637	15.648	−0.069
290.000	6.372	18.093	18.133	−0.222
300.000	10.986	18.055	18.074	−0.102
310.000	15.646	18.011	18.021	−0.056
320.000	20.386	17.984	17.986	−0.011
330.000	25.162	17.964	17.958	0.031
340.000	29.947	17.945	17.932	0.073
280.000	6.303	20.159	20.175	−0.082
290.000	12.479	20.103	20.110	−0.030
300.000	18.689	20.059	20.056	0.018
310.000	24.980	20.034	20.021	0.064
320.000	31.289	20.012	19.992	0.100
265.000	5.017	22.078	22.079	−0.004
270.000	9.062	22.049	22.046	0.014
275.000	13.039	22.011	22.009	0.012
280.000	17.025	21.983	21.975	0.033
285.000	21.091	21.964	21.955	0.042
290.000	25.177	21.950	21.938	0.052
295.000	29.265	21.937	21.923	0.062
300.000	33.347	21.925	21.909	0.071
245.000	3.729	24.172	24.142	0.126
250.000	9.092	24.138	24.108	0.126
255.000	14.264	24.091	24.063	0.116
260.000	19.558	24.062	24.036	0.111
265.000	24.966	24.044	24.019	0.105
270.000	30.383	24.028	24.004	0.101
275.000	35.794	24.014	23.991	0.096
225.000	6.774	26.173	26.155	0.071
230.000	13.424	26.119	26.103	0.060
235.000	20.245	26.083	26.068	0.057
240.000	27.343	26.061	26.051	0.039
245.000	34.465	26.043	26.037	0.023

peratures, pressures, and densities on a total of 15 isochores ranging from 1.0 to 26 mol · dm^{-3}. The experimental temperatures range from 225 to 400 K, and pressures extend to 36 MPa. Sample masses ranged from 1.3 to 32 g. Figure 6 illustrates the pressure and temperature ranges of the data. Also included in Table II are deviations of the densities from those estimated by Ely [8] with corresponding states. Figure 7 shows the deviations of selected representative isochores. The isochores depicted are at reduced densities (ρ/ρ_c) of approximately 0.25, 0.8, 1.4, and 2.6 and are typical of dilute vapor, near-critical vapor, near-critical liquid, and compressed liquid isochores, respectively. As shown by Fig. 7, the model accurately predicts density better than 0.15% at densities $>2\rho_c$. At lower densities, the model tends to predict densities that are too low by up to 0.5%; the largest deviations are near the critical density. The overall RMS deviation between the predicted and the experimental values was 0.37%.

As illustrated by Fig. 7, the model has both strengths and weaknesses. While densities of compressed liquid states ($\rho > 2\rho_c$) are accurately predicted, small systematic deviations occur at low and at moderate densities. When density deviations are plotted at a constant temperature (i.e., 320 K) we have observed an S-shaped pattern. This trend is typical of predictions from a model when an analytic equation of state is used as a reference fluid equation. Near the critical, these equations predict $P-\rho$ isotherms which are not as flat as experimental data demands. It is not surprising, then, that the model developed by Ely [8] with a 32-term modified Benedict–Webb–Rubin equation of state for pure CO_2 also demonstrates this point. Thus if we want to improve the picture in the critical region, we should develop a

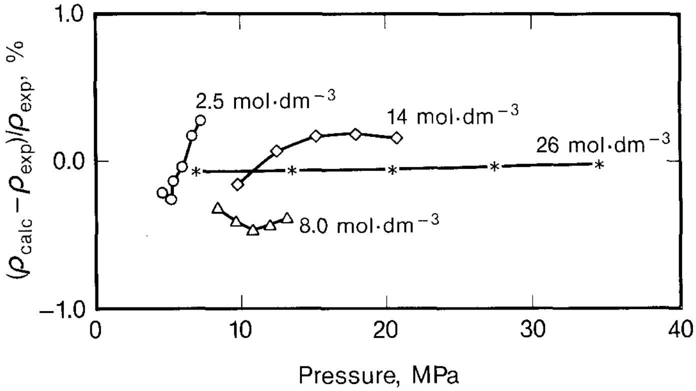

Fig. 7. Deviations of ($0.98\,CO_2 + 0.02\,CH_4$) densities calculated with corresponding-states model [8] from this work, for four densities, nominally 0.25, 0.8, 1.4, and 2.6 times the mixture critical density.

new model which uses a reference equation whose properties are such that flatter $P-\rho$ isotherms will be predicted by the equation. This work is now in progress in our laboratories.

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