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PVT of Toluene at Temperatures to 673 K

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Measurements of the *PVT* behavior of compressed gaseous and liquid toluene are reported. Pressure versus temperature observations were made along paths of very nearly constant density (pseudoisochores) in the temperature range from about 348 to over 673 K and at pressures to about 35 MPa. Twenty-seven pseudoisochores were determined ranging in density from about 1.7 to near 9 mol/dm^3.

Introduction

Measurements of the *PVT* behavior of compressed toluene are reported for the temperature range from about 348 to over 673 K at pressures to about 35 MPa. Pressure versus temperature observations were made along paths of nearly constant density (pseudoisochores). Twenty-seven pseudoisochores were determined ranging in density from 1.7 to about 9 mol/dm^3.

Experiment

The reagent grade toluene used in this study was analyzed by gas chromatography. Small quantities (less than 0.07%) of benzene, ethylbenzene, and thiophene were found to be present. Purification with sulfuric acid, followed by distillation, reduced the impurity level to less than 0.001%. The major remaining impurity was benzene which was present at this low level regardless of the lot of starting material.

Measurements were made using an automated high-temperature *PVT* apparatus, which has been described in detail (*1*). Measurements were made by confining the toluene samples in a thick-walled, very nearly constant volume, stainless steel cell and measuring the pressure as a function of temperature to define the locus of *PT* points along paths of very nearly constant density. Cell temperatures were determined with a platinum resistance thermometer calibrated, with respect to the IPTS-1968, by the National Bureau of Standards. Pressures were determined from the frequency of a commercial vibrating quartz pressure transducer calibrated frequently against a primary dead weight gauge and are estimated accurate to the greater of 10 kPa or 0.05%. At the completion of a series of *PT* observations (a run) the toluene samples were condensed into a detachable cylinder, held at liquid nitrogen temperature, for subsequent weighing to determine the number of moles of sample in the system during the measurements. Densities assigned to each *PT* point were then calculated from the calibrated volumes of the system. Small corrections were made for thermal expansion and pressure dilation of the cell and for the small quantities of fluid residing in the various noxious volumes.

Table I. Decomposition Products Detected in Toluene[a]

compound	mol %
dimethylbiphenyl	15.0
stilbene	5.7
diphenylmethane	4.8
methylbiphenyl	4.8
benzene	1.4
benzyltoluene	1.3
dibenzyl	0.5
biphenyl	0.1
fluorene	0.1
anthracene	0.1
pnenathrene	0.1
unidentified components	0.1
toluene	balance

[a] Toluene at 723 K, 15 MPa, for 48 h.

Results and Discussion

The maximum temperature for the initial run reached 723 K; however, decomposition and reaction of the toluene became severe at the highest temperature, as was evidenced by an unacceptable increase in the measured pressure with time. Measurements on a sample at a density of approximately 4 mol/dm^3, held at a temperature of 723 K for 24 h, exhibited a pressure rise of over 20 kPa/h and showed no signs of approaching equilibrium. Results of an analysis of a sample of toluene held for 48 h at 723 K and a pressure of 15 MPa are shown in Table I. Chemical denaturation of the toluene was found to increase appreciably at temperatures above 643 K with ethylbenzene being the main reaction product. An upper limit of 673 K was set for the *PVT* measurements, however, since the pressure increase with time at this temperature was found to be sufficiently small (0.6 kPa/h for the 4 mol/dm^3 test sample) and the residence time for the sample at temperatures over 643 K was normally less than about 8 h. The resulting pressure error due to toluene reaction is probably less than 6.0 kPa and is within the normal uncertainty in the pressure measurements. After each run, the contents of the *PVT* cell were analyzed by gas chromatography and found to be essentially identical with the starting samples.

Table II. *PVT* Data for Toluene

T, K	P, MPa	density, mol/dm^3
583.12	3.5577	1.458
593.17	3.7749	1.458
603.16	3.9844	1.457
613.21	4.1902	1.456
623.11	4.3907	1.455
633.10	4.5892	1.454
643.12	4.7859	1.454
653.16	4.9805	1.453
663.18	5.1726	1.452
673.12	5.3628	1.451
583.16	3.6886	1.780
593.18	3.9863	1.779
603.17	4.2558	1.778
613.19	4.5189	1.777
623.13	4.7757	1.776
633.11	5.0293	1.775
643.19	5.2813	1.774
653.19	5.5293	1.773
663.16	5.7749	1.772
673.14	6.0185	1.771
583.14	3.6893	2.258
583.05	3.6804	2.258
593.10	4.1278	2.257
603.15	4.4926	2.255
613.16	4.8471	2.254
623.13	5.1949	2.253
633.13	5.5399	2.252
643.13	5.8810	2.250
653.16	6.2197	2.249
663.19	6.5560	2.248
673.16	6.8896	2.247
583.16	3.6914	2.831
593.18	4.1689	2.830
603.18	4.6308	2.828
613.19	5.0882	2.827
623.19	5.5438	2.825
633.18	5.9979	2.823
643.12	6.4498	2.822
653.18	6.9040	2.820
663.18	7.3553	2.819
673.11	7.8045	2.817
583.10	3.6916	3.371
593.16	4.1791	3.370
603.14	4.7277	3.368
613.11	5.2899	3.366
623.16	5.8606	3.364
633.13	6.4344	3.362
643.12	7.0119	3.360
653.17	7.5928	3.358
663.15	8.1746	3.357
673.16	8.7567	3.355
583.12	3.6914	3.668
593.15	4.1873	3.666
603.15	4.8009	3.664
613.17	5.4380	3.662
623.14	6.0848	3.660
633.18	6.7427	3.658
643.17	7.4050	3.656
653.16	8.0708	3.654
663.12	8.7388	3.652
673.17	9.4118	3.650
583.11	3.6887	3.682
593.12	4.1838	3.680
603.16	4.7995	3.678
613.12	5.4357	3.676
623.11	6.0853	3.674
633.12	6.7441	3.672
583.11	3.6892	3.711
593.13	4.1862	3.709
603.16	4.8073	3.707
613.17	5.4521	3.705
623.10	6.1081	3.703
633.13	6.7740	3.701
643.08	7.4445	3.699
653.17	8.1239	3.697
603.15	4.9148	3.808
613.16	5.6376	3.806
623.19	6.3760	3.803
633.15	7.1245	3.801
643.13	7.8800	3.799
653.12	8.6425	3.797
663.16	9.4102	3.795
673.12	10.1796	3.793
683.15	10.9554	3.791
693.15	11.7304	3.789
703.13	12.5062	3.786
713.15	13.2851	3.784
723.18	14.0684	3.782
603.15	4.9113	3.972
613.18	5.6351	3.969
623.18	6.3737	3.967
633.11	7.1206	3.965
643.14	7.8796	3.963
653.13	8.6424	3.961
663.13	9.4103	3.958
583.16	3.6918	4.121
593.17	4.2500	4.119
603.16	4.9948	4.117
613.18	5.7684	4.114
623.11	6.5568	4.112
633.14	7.3597	4.110
643.15	8.1708	4.108
653.13	8.9871	4.105
663.20	9.8129	4.103
673.18	10.6385	4.101
583.12	3.6920	4.559
593.17	4.4921	4.556
603.14	5.4200	4.554
613.18	6.3769	4.551
623.15	4.3466	4.549
633.17	8.3333	4.546
643.19	9.3280	4.544
653.17	10.3302	4.541
663.19	11.3378	4.539
673.18	12.3485	4.536
583.15	3.8303	4.845
593.16	4.8847	4.843
603.17	5.9729	4.840
613.18	7.0834	4.837
623.10	8.2060	4.834
633.18	9.3494	4.832
643.20	10.4978	4.829
653.17	11.6507	4.826
663.12	12.8086	4.823
673.13	13.9690	4.821
583.19	4.2981	5.120
593.17	5.5275	5.117
603.18	6.7846	5.114
613.11	8.0552	5.111
623.15	9.3453	5.108
633.17	10.6450	5.105
643.14	11.9501	5.102
653.15	13.2596	5.100
663.14	14.5743	5.097
673.16	15.8961	5.094
563.18	4.1958	5.372
573.11	5.9699	5.369
583.14	7.7705	5.366
593.18	9.5902	5.363
603.18	11.4140	5.360
613.19	13.2439	5.357
623.14	15.0744	5.353
633.16	16.9141	5.350
643.19	18.7557	5.347
653.20	20.5952	5.344
663.17	22.4293	5.341
673.11	24.2631	5.338
573.14	4.0896	5.491
583.17	5.5733	5.488
593.14	7.0832	5.485
603.17	8.6113	5.482
613.15	10.1501	5.479
623.14	11.6982	5.475
633.12	13.2546	5.472
643.13	14.8161	5.469
653.18	16.3829	5.466
663.12	17.9457	5.463
673.18	19.5147	5.460
563.18	3.9936	5.801
573.16	5.7390	5.798
583.14	7.5048	5.795
593.14	9.2864	5.791
603.13	11.0820	5.788
613.17	12.8859	5.784
623.19	14.6922	5.781
633.17	16.4974	5.778
643.17	18.3072	5.775
653.13	20.1164	5.771
663.17	21.9269	5.768
673.15	23.7321	5.765
548.19	2.9015	6.059
553.15	3.8837	6.057
563.14	5.8741	6.053
573.14	7.8810	6.050
583.18	9.9075	6.046
593.18	11.9397	6.043
603.15	13.9778	6.039
613.11	16.0137	6.036
613.10	16.0123	6.036
623.16	18.0568	6.032
633.15	20.0972	6.029
643.13	22.1343	6.025
653.18	24.1707	6.022
663.10	26.1984	6.018
673.15	28.2273	6.015
543.09	2.3150	6.099
553.06	4.2834	6.095
563.12	6.3469	6.091
573.10	8.4088	6.088
583.12	10.4828	6.084
593.11	12.5596	6.080
603.09	14.6381	6.077
613.13	16.7136	6.073
623.12	18.7800	6.070
633.14	20.8421	6.066
643.19	22.8886	6.063
543.15	2.3762	6.121
548.15	3.3929	6.119
553.11	4.4096	6.117
563.14	6.4783	6.113
573.11	8.5542	6.110
583.14	10.6484	6.106
583.13	10.6465	6.106
593.16	12.7507	6.103
603.16	14.8518	6.099
613.19	16.9586	6.096
623.11	19.0535	6.092
633.16	21.1619	6.089
643.17	23.2628	6.085
653.16	25.3564	6.082
538.18	2.2681	6.235
543.15	3.3148	6.233
548.12	4.3914	6.231
553.19	5.4857	6.229
563.19	7.6771	6.225
573.17	9.8798	6.222
583.19	12.0922	6.218
593.15	14.3045	6.214
603.17	16.5227	6.211
613.14	18.7373	6.207
623.16	20.9497	6.204
633.15	23.1567	6.200
643.17	25.3659	6.197
653.16	27.5656	6.193
663.19	29.7640	6.189
673.17	31.9501	6.186
533.17	2.5067	6.377
538.16	3.6536	6.375
543.17	4.8179	6.373
548.16	5.9907	6.371
553.15	7.1678	6.369
563.17	9.5331	6.365
573.18	11.9013	6.361
583.16	14.2739	6.358
593.17	16.6512	6.354
603.17	19.0276	6.350
613.15	21.3962	6.347
623.18	23.7600	6.343
633.14	26.1171	6.339
643.16	28.4686	6.336
653.13	30.8113	6.332
663.15	33.1486	6.329
523.15	1.6498	6.529
528.18	2.7338	6.505
533.20	3.9804	6.503
538.18	5.2291	6.501
543.10	6.4750	6.499
548.11	7.7344	6.497
553.14	8.9949	6.495
563.19	11.5234	6.491
573.13	14.0441	6.487
583.12	16.5703	6.483
593.18	19.1011	6.479
593.19	19.0984	6.479
603.11	21.6147	6.476
613.18	24.1338	6.472
623.19	26.6383	6.468
633.18	29.1327	6.465
643.17	31.6198	6.461
653.13	34.0943	6.457
493.11	1.7313	7.063
498.12	3.2094	7.060
503.19	4.8835	7.058
508.12	6.5365	7.056
513.17	8.2096	7.054
518.15	9.8704	7.051
523.12	11.5294	7.049
528.12	13.1931	7.047
533.15	14.5877	7.045
538.16	16.5148	7.043
543.13	18.1677	7.041
548.09	19.8091	7.039
553.12	21.4632	7.037
563.10	24.7472	7.033
573.11	28.0262	7.028
583.14	31.2855	7.024
593.11	34.5272	7.020
438.12	1.2384	7.819
443.18	3.0870	7.794
448.16	5.5193	7.791
453.18	7.9506	7.789
458.11	10.3625	7.786
463.14	12.7867	7.783
468.18	15.2041	7.781
473.11	17.5960	7.779
463.20	12.7928	7.783
468.19	15.2056	7.781
473.18	17.6010	7.778
478.11	19.9856	7.776
483.16	22.3832	7.774
488.10	24.7457	7.771
493.16	27.1277	7.769
498.20	29.4905	7.767
503.16	31.8336	7.764
508.19	34.1761	7.762
403.16	1.4425	8.269
408.18	3.7239	8.244
413.17	6.7377	8.241
418.11	9.7286	8.238
423.18	12.7346	8.235
428.17	15.7220	8.232
418.05	9.7207	8.238
423.19	12.7417	8.235
428.17	15.7211	8.232

Table II (Continued)

T, K	P, MPa	density, mol/dm^3	T, K	P, MPa	density, mol/dm^3	T, K	P, MPa	density, mol/dm^3	T, K	P, MPa	density, mol/dm^3
433.19	18.6962	8.230	453.17	30.4280	8.219	353.07	2.2504	8.809	373.09	18.2739	8.796
438.18	21.6547	8.227	458.10	33.3214	8.217	358.07	6.2757	8.806	378.19	22.2461	8.793
443.16	24.5948	8.224	463.11	36.2038	8.214	363.12	10.3007	8.803	383.19	26.1591	8.790
448.10	27.5120	8.222	348.07	0.2102	8.836	368.21	14.3434	8.799	388.09	30.0139	8.788

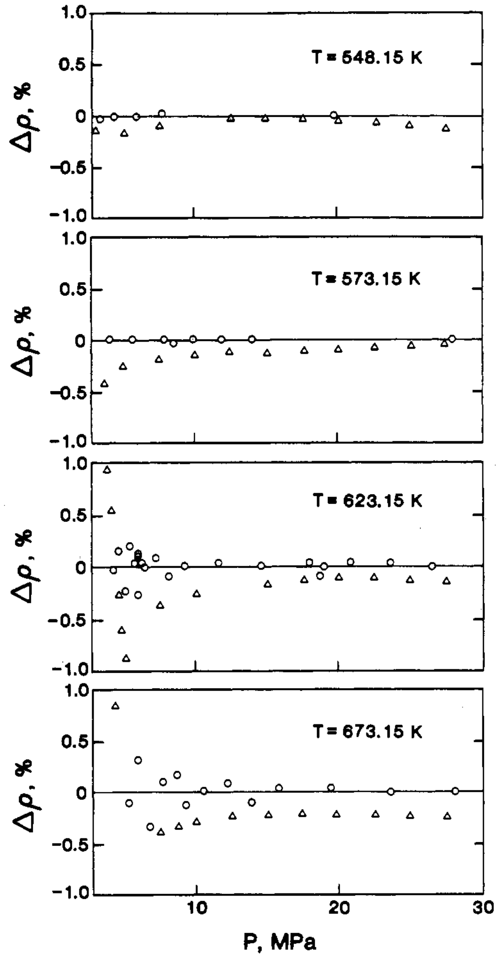

Figure 1. Density differences between the data of ref *2* (△) and this work (○) are shown along selected isotherms. For the 623.15 K isotherm, five out-of-range points are not plotted. Densities and their percent deviations are (3.1, 1.86%), (3.6, 1.42%), (5.4, −1.04%), (5.6, −1.21%), (5.8, −1.44%), respectively. Data are plotted relative to polynomial fits to the data of this work.

Table III. Comparison of Representative Toluene Densities with Literature Values (Interpolated) in the Dense Liquid Region

		density, mol/dm^3				
T, K	P, MPa	this work	ref *2*	density dev, %	ref *3*	density dev, %
373.15	18.274	8.796	8.809	+0.15	8.802	+0.07
423.15	12.742	8.235	8.227	−0.10	8.227	−0.10
473.15	17.596	7.778	7.796	+0.23	7.789	+0.14
523.15	11.529	7.049	7.047	−0.03	7.021	−0.40

Except for the critical region, density uncertainties for the toluene measurements are estimated to range from about ±0.2% at high densities to ±0.3% at the lowest density. This is due largely to the combined uncertainty in the calibrated volumes of about ±0.1% and the uncertainty in the measured sample weight which could reach about ±0.2% for the lowest sample weights. This corresponds to a weighing uncertainty of 0.005% in the total combined weight for the lowest density sample consisting of about 0.016 kg of toluene sample and 0.6 kg tare for the weighing cylinder. In the critical region, pressure uncertainty and an estimated temperature uncertainty of about ±0.1 K can contribute significantly to errors in the assigned density values.

The *PVT* data from the present work are tabulated in Table II. Only the isotherm data of Akhundov and Abdullaev (*2*) from 273 to 673 K and the limited data of Kragas and Kobayashi (*3*) from 323 to 523 K are available for comparison with the data of this work. Comparisons with the data of ref *2* are shown in Figure 1. Agreement between the data sets is generally better than 0.4% in density except in the critical region where differences are as large as a few percent. Typical density differences at lower temperatures, obtained by interpolation from ref *2* and *3*, are tabulated in Table III.

These data and toluene data from other available sources are currently undergoing extensive correlation and critical evaluation in this laboratory for the purpose of formulating an accurate, wide range equation of state suitable for calculation of thermodynamic properties of toluene (*4*).

Registry No. Toluene, 108-88-3.

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