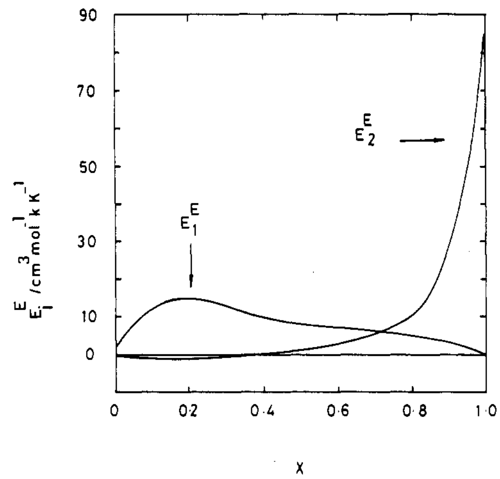

Figure 3. Partial molar excess thermal expansibilities E_1^E and E_2^E against mole fraction of water at 298.15 K.

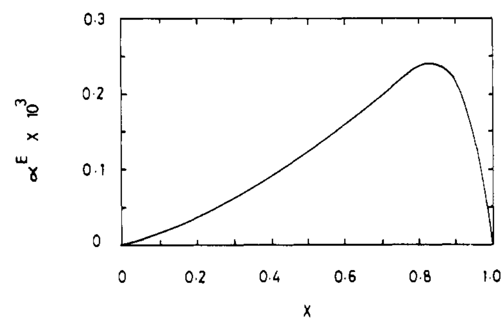

Figure 4. Coefficient of thermal expansion α^E against mole fraction of water at 298.15 K.

behavior is similar to that found (*3-6*) in aqueous mixtures with liquids such as dimethylformamide, dimethyl sulfoxide, tetrahydrofuran, and acetonitrile. The general explanation (*7*) applicable in this case, is that hydrogen bonding to the carbonyl group is stronger than to water, so that the solute enhances structure and close packing in the disordered regions.

Excess partial molar volumes are illustrated in Figure 2. It is interesting that the largest negative V_2^E occurs at a lower mole fraction of γ-butyrolactone, but that with further addition of γ-butyrolactone V_2^E decreases rapidly until about $x = 0.6$ and then gradually approaches its ideal value. This suggests that larger amounts of γ-butyrolactone disrupt the structure and thereby V_2^E decrease.

It may observed that on addition of γ-butyrolactone the E_i^E (Figure 3) and α^E (Figure 4) show that close packing is a maximum at low mole fraction of γ-butyrolactone ($x \leq 0.2$) as expected from thermal disruption of the water ice I structure.

Glossary

a_1, a_2, a_j	coefficients in representation of excess molar volume by eq 1
E_i^E	partial molar excess expansibilities
k	number of coefficients in eq 1
s	standard deviation
T	thermodynamic temperature, K
V_m^E	molar excess volume, $cm^3\ mol^{-1}$
V_i^E	excess partial molar volume
V_m	molar volume of the mixture
x	mole fraction of water

Greek Letters

α_1^*	thermal expansion coefficient of pure water
α^E	excess thermal expansion coefficient
ϕ_1	volume fraction of pure water

Registry No. γ-Butyrolactone, 96-48-0.

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PVT Measurements on Benzene at Temperatures to 723 K

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Measurements of the *PVT* behavior of compressed gaseous and liquid benzene are reported. Pressure vs. temperature observations were made along paths of very nearly constant density (pseudoisochores) in the temperature range from about 425 K to over 720 K and at pressures to about 35 MPa. Twenty-four pseudoisochores were determined ranging in density from about 1 mol/dm^3 to over 9 mol/dm^3.

Introduction

Although *PVT* data for benzene are available from a number of sources (*1-5*), data remain scarce at elevated temperatures, particularly above the critical temperature. The *P-T* loci of the principal benzene data are shown in Figure 1. Only the data of Gehrig and Lentz (*4*) and Gornowski et al. (*3*) are available above about 590 K, and those of ref *3* are limited to low densities. We report new measurements of the *PVT* behavior of compressed gaseous and liquid benzene in the temperature range from about 425 K to over 720 K at pressures to about 35 MPa. Pressure vs. temperature observations were made along paths of nearly constant density (pseudoisochores). Twenty-four pseudoisochores were determined ranging in density from about 1 mol/dm^3 to 9 mol/dm^3.

Experiment

Measurements were made using an automated high-temperature *PVT* apparatus which has been described in detail (*6*).

Table I. Density, Pressure, and Temperature Data for Benzene

den, mol/dm^3	T, K	P, MPa	den, mol/dm^3	T, K	P, MPa	den, mol/dm^3	T, K	P, MPa	den, mol/dm^3	T, K	P, MPa
1.253	533.185	3.318	2.807	613.129	7.026	4.449	693.154	15.123	5.741	653.072	16.891
1.252	543.157	3.481	2.806	623.111	7.432	4.447	703.184	15.917	5.741	653.190	16.896
1.252	553.141	3.624	2.804	633.126	7.836	4.444	713.098	16.705	5.738	663.106	18.181
1.251	563.126	3.775	2.803	643.101	8.237	4.442	723.157	17.499	5.738	663.185	18.187
1.250	573.138	3.924	2.801	653.170	8.637	5.101	563.110	5.071	5.735	673.153	19.475
1.250	583.157	4.072	2.799	663.160	9.033	5.098	573.107	5.987	5.735	673.166	19.477
1.249	593.181	4.220	2.798	673.115	9.426	5.095	583.146	6.936	5.731	683.091	20.760
1.248	603.198	4.366	2.796	683.168	9.820	5.092	593.154	7.905	5.731	683.187	20.766
1.247	613.141	4.509	2.795	693.108	10.209	5.089	603.158	8.885	5.728	693.117	22.049
1.247	623.143	4.651	2.793	703.175	10.600	5.086	613.179	9.875	5.728	693.125	22.051
1.246	633.191	4.792	2.792	713.196	10.988	5.083	623.102	10.866	5.725	703.143	23.338
1.245	643.184	4.932	2.790	723.187	11.374	5.080	633.118	11.869	5.725	703.176	23.339
1.245	653.149	5.070	3.232	563.052	4.943	5.077	643.136	12.876	5.722	713.157	24.623
1.244	663.165	5.207	3.230	573.161	5.442	5.074	653.160	13.884	5.722	713.160	24.625
1.243	673.173	5.344	3.228	583.169	5.925	5.071	663.180	14.894	5.718	723.120	25.907
1.243	683.155	5.480	3.226	593.056	6.399	5.069	673.146	15.903	5.718	723.140	25.902
1.242	693.168	5.615	3.224	603.139	6.876	5.066	683.150	16.912	6.063	563.115	6.061
1.241	703.156	5.749	3.223	613.143	7.347	5.063	693.159	17.922	6.060	573.124	7.437
1.669	573.209	4.556	3.221	623.126	7.815	5.060	703.131	18.930	6.056	583.119	8.834
1.668	583.111	4.773	3.219	633.159	8.282	5.057	713.151	19.939	6.053	593.121	10.248
1.667	593.177	4.987	3.217	643.108	8.745	5.054	723.169	20.946	6.049	603.144	11.674
1.666	603.191	5.198	3.215	653.162	9.208	5.149	563.142	5.086	6.046	613.142	13.105
1.665	613.173	5.406	3.214	663.178	9.668	5.147	568.128	5.548	6.042	623.125	14.546
1.665	623.110	5.612	3.212	673.183	10.126	5.146	573.180	6.025	6.039	633.155	15.991
1.664	633.154	5.816	3.210	683.142	10.581	5.144	578.123	6.505	6.035	643.181	17.437
1.663	643.162	6.018	3.208	693.160	11.036	5.143	583.117	6.992	6.032	653.177	18.883
1.662	653.178	6.218	3.206	703.182	11.488	5.141	588.120	7.485	6.028	663.146	20.327
1.661	663.124	6.416	3.205	713.169	11.939	5.140	593.112	7.981	6.025	673.174	21.775
1.660	673.184	6.614	3.203	723.169	12.388	5.138	598.122	8.482	6.021	683.177	23.220
1.659	683.186	6.810	3.538	563.193	4.967	5.137	603.178	8.987	6.018	693.170	24.660
1.658	693.178	7.004	3.536	573.131	5.510	5.135	608.168	9.491	6.015	703.183	26.101
1.657	703.154	7.197	3.534	583.096	6.047	5.134	613.135	9.995	6.011	713.172	27.540
1.656	713.114	7.389	3.532	593.116	6.582	5.132	618.133	10.504	6.373	543.117	3.882
1.655	723.151	7.580	3.530	603.125	7.115	5.131	623.160	11.015	6.371	548.178	4.630
1.995	553.095	4.320	3.528	613.127	7.646	5.128	633.181	12.040	6.369	553.142	5.387
1.994	558.146	4.470	3.526	623.099	8.174	5.125	643.143	13.066	6.367	558.114	6.152
1.994	563.169	4.615	3.524	633.149	8.703	5.122	653.164	14.098	6.366	563.100	6.927
1.993	573.096	4.895	3.522	643.180	9.230	5.119	663.146	15.129	6.364	568.176	7.715
1.992	583.095	5.169	3.520	653.162	9.755	5.116	573.157	16.163	6.362	573.159	8.501
1.991	593.109	5.439	3.518	663.163	10.277	5.505	563.094	5.278	6.358	583.123	10.089
1.989	603.158	5.705	3.516	673.149	10.798	5.502	573.160	6.361	6.354	593.139	11.691
1.988	613.145	5.967	3.514	683.190	11.320	5.499	583.092	7.466	6.350	603.170	13.300
1.987	623.097	6.228	3.512	693.155	11.837	5.496	593.112	8.594	6.347	613.125	14.911
1.986	633.136	6.485	3.510	703.147	12.354	5.492	603.113	9.733	6.343	623.128	16.530
1.985	643.123	6.739	3.508	713.181	12.871	5.489	613.133	10.884	6.339	633.150	18.153
1.984	653.197	6.993	3.506	723.087	13.383	5.486	623.106	12.038	6.336	643.179	19.777
1.983	663.173	7.243	4.060	563.107	4.971	5.483	633.131	13.201	6.332	653.135	21.394
1.982	673.170	7.491	4.057	573.096	5.616	5.480	643.121	14.367	6.328	663.173	23.019
1.981	683.183	7.738	4.055	583.100	6.274	5.477	653.095	15.534	6.325	673.121	24.634
1.980	693.164	7.984	4.053	593.102	6.939	5.473	663.172	16.708	6.522	543.136	4.224
1.978	703.194	8.228	4.050	603.154	7.610	5.470	673.151	17.878	6.518	553.115	5.846
1.977	713.184	8.470	4.048	613.147	8.281	5.467	683.160	19.049	6.514	563.136	7.503
1.976	723.131	8.711	4.046	623.101	8.952	5.464	693.175	20.219	6.510	573.093	9.173
2.313	558.086	4.617	4.044	633.100	9.626	5.461	703.149	21.387	6.506	583.127	10.866
2.313	563.115	4.794	4.041	643.145	10.302	5.458	713.133	22.553	6.502	593.109	12.565
2.311	573.105	5.135	4.039	653.181	10.978	5.455	723.177	23.720	6.498	603.090	14.272
2.310	583.115	5.467	4.037	663.148	11.650	5.773	558.170	4.959	6.494	613.123	15.989
2.309	593.100	5.792	4.034	673.143	12.326	5.773	558.197	4.951	6.490	623.118	17.706
2.308	603.151	6.115	4.032	683.118	12.998	5.771	563.088	5.538	6.487	633.116	19.425
2.306	613.136	6.432	4.030	693.179	13.672	5.771	563.111	5.535	6.483	643.115	21.144
2.305	623.108	6.745	4.028	703.166	14.342	5.768	573.111	6.742	6.479	653.108	22.860
2.304	633.110	7.056	4.025	713.114	15.010	5.768	573.124	6.744	6.476	663.122	24.575
2.302	643.102	7.364	4.023	723.120	15.680	5.764	583.114	7.974	6.472	673.148	26.287
2.301	653.121	7.671	4.482	563.117	4.979	5.764	583.217	7.980	6.468	683.160	27.998
2.300	663.120	7.975	4.480	573.096	5.709	5.761	593.120	9.223	6.465	693.194	29.707
2.299	673.206	8.278	4.477	583.111	6.463	5.761	593.172	9.224	6.461	703.177	31.406
2.297	683.156	8.577	4.475	593.111	7.231	5.758	603.147	10.487	6.457	713.183	33.103
2.296	693.181	8.876	4.472	603.101	8.008	5.758	603.171	10.486	6.454	723.129	34.785
2.295	703.183	9.173	4.470	613.154	8.792	5.754	613.139	11.755	6.806	538.082	4.281
2.293	713.183	9.468	4.467	623.108	9.576	5.754	613.155	11.759	6.804	543.109	5.202
2.292	723.185	9.761	4.465	633.119	10.366	5.751	623.108	13.034	6.802	548.142	6.127
2.815	563.146	4.921	4.462	643.171	11.159	5.751	623.129	13.034	6.800	553.104	7.052
2.814	573.142	5.359	4.460	653.165	11.952	5.748	633.122	14.319	6.796	563.141	8.927
2.812	583.133	5.784	4.457	663.182	12.746	5.748	633.131	14.316	6.792	573.107	10.812
2.810	593.117	6.202	4.454	673.183	13.539	5.744	643.176	15.605	6.788	583.110	12.712
2.809	603.129	6.616	4.452	683.167	14.331	5.744	643.200	15.611	6.784	593.136	14.621

Table I (Continued)

den, mol/dm^3	T, K	P, MPa	den, mol/dm^3	T, K	P, MPa	den, mol/dm^3	T, K	P, MPa	den, mol/dm^3	T, K	P, MPa
6.780	603.180	16.539	7.102	543.134	6.884	7.758	508.175	3.856	533.110	8.395	23.036
6.776	613.132	18.445	7.100	548.153	7.943	7.755	513.181	5.229	543.137	8.390	26.610
6.772	623.138	20.361	7.098	553.131	9.003	7.752	518.114	6.598	553.115	8.385	30.159
6.768	633.087	22.268	7.096	558.160	10.070	7.750	523.182	7.984	563.202	8.380	33.709
6.764	643.147	24.180	7.094	563.133	11.134	7.747	528.127	9.359	443.165	8.999	0.886
6.760	653.198	26.092	7.091	568.121	12.203	7.745	533.108	10.742	448.145	8.994	2.845
6.756	663.170	27.988	7.089	573.178	13.279	7.743	538.151	12.130	453.121	8.968	4.839
6.752	673.179	29.887	7.087	578.125	14.346	7.740	543.183	13.520	458.164	8.965	7.128
6.749	683.168	31.776	7.085	583.132	15.422	7.738	548.138	14.900	463.118	8.962	9.397
6.745	693.188	33.667	7.083	588.132	16.498	7.738	548.137	14.904	468.166	8.959	11.679
7.002	528.138	3.226	7.081	593.162	17.575	7.735	553.059	16.278	473.169	8.956	13.943
7.000	533.117	4.207	7.079	598.118	18.646	7.735	553.125	16.287	478.112	8.953	16.195
6.998	538.155	5.200	7.077	603.117	19.723	7.733	558.127	17.674	483.171	8.950	18.458
6.995	543.185	6.203	7.075	608.126	20.797	7.731	563.115	19.057	488.140	8.947	20.696
6.993	548.192	7.209	7.073	613.119	21.870	7.728	568.159	20.444	493.117	8.944	22.934
6.991	553.118	8.215	7.071	618.138	22.944	7.726	573.152	21.822	498.141	8.942	25.169
6.989	558.136	9.233	7.069	623.167	24.018	7.722	583.121	24.580	503.153	8.939	27.400
6.987	563.150	10.253	7.441	508.160	2.453	7.717	593.129	27.329	508.125	8.936	29.610
6.985	568.122	11.272	7.439	513.117	2.638	7.713	603.176	30.074	513.136	8.934	31.823
6.982	573.159	12.301	7.414	518.169	3.525	7.708	613.174	32.794	518.162	8.931	34.032
6.978	583.161	14.359	7.411	523.107	4.667	7.704	623.125	35.506	423.155	9.363	1.077
6.974	593.112	16.414	7.407	533.117	7.053	8.451	473.147	1.696	428.144	9.336	3.101
6.970	603.167	18.479	7.402	543.096	9.454	8.425	478.174	3.181	433.154	9.332	5.723
6.966	613.177	20.540	7.397	553.117	11.870	8.422	483.175	4.992	438.157	9.329	8.370
6.962	623.127	22.595	7.393	563.118	14.289	8.419	488.169	6.801	443.118	9.326	11.005
6.958	633.176	24.655	7.388	573.103	16.711	8.416	493.188	8.616	448.153	9.322	13.644
6.954	643.140	26.697	7.384	583.105	19.135	8.414	498.187	10.429	453.164	9.319	16.266
6.950	653.150	28.745	7.380	593.105	21.555	8.411	503.128	12.229	458.130	9.316	18.870
6.946	663.124	30.783	7.376	603.109	23.974	8.408	508.176	14.043	463.160	9.313	21.480
6.942	673.158	32.821	7.371	613.201	26.398	8.405	513.112	15.838	468.139	9.310	24.068
7.133	523.141	2.968	7.367	623.119	28.791	8.403	518.106	17.643	473.125	9.307	26.649
7.109	528.152	3.770	7.363	633.115	31.187	8.400	523.110	19.439	478.161	9.304	29.226
7.107	533.167	4.792	7.359	643.115	33.572	8.398	528.119	21.243	483.111	9.302	31.780
7.105	538.156	5.836	7.783	503.175	2.644						

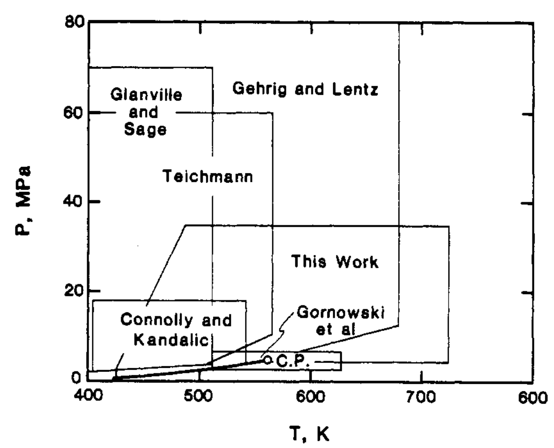

Figure 1. Locus of principal $P-T$ data for benzene from various sources (ref *1–5*).

Measurements were made by confining the benzene 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 $P-T$ points along paths of very nearly constant density. Cell temperatures were determined by using 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 against a commerical dead weight gauge, and are estimated to be accurate to the greater of 10 kPa or 0.05%. At the completion of a series of PT observations (a run), the benzene samples were condensed into a detachable cylinder held at the normal boiling temperature of liquid nitrogen for subsequent weighing to determine the number of moles of sample in the system. Densities assigned to each PT point were then calculated from the number of moles and the calibrated volumes of the system. Small corrections were made for thermal expansion, for pressure dilation of the cell, and for the small quantities of fluid residing in the various volumes external to the cell.

Specially prepared spectrochemical grade benzene was used in this work. Gas chromatography revealed the presence of significant amounts (approaching 0.3%) of both organic impurities (including some sulfur compounds) and water. The benzene was therefore purified by washing with concentrated sulfuric acid, followed by several washings with distilled water. This process was repeated until no yellow coloration was observed in the acid layer. The water was then removed by azeotropic distillation over sodium, with the water-rich fraction coming off below 80 °C. The benzene was then stored over activated 5A molecular seives. Benzene, thus prepared, showed no detectable impurities at concentrations above 2 ppm.

Results and Discussion

The maximum temperature for the initial runs was kept below 623 K. Maximum temperature for subsequent runs was increased to 677 K and then to 723 K to determine the onset of thermal degradation of the samples. After each run, the contents of the PVT cell were analyzed by gas chromatography. A single decomposition product was detected whenever the temperature was maintained above about 650 K during the course of a measurement. The impurity concentrations ranged from 0.02% to as high as 0.08%, the highest level being observed when the cell temperature reached the maximum measurement temperature of 723 K. The decomposition product was identified, using infrared spectroscopy and gas chromatography retention volume comparison, as biphenyl.

In order to determine the effect of the decomposition on the measured pressures, some runs, extending to the maximum temperature, were traversed twice. The measured pressures were found to be identical within the precision of the mea-

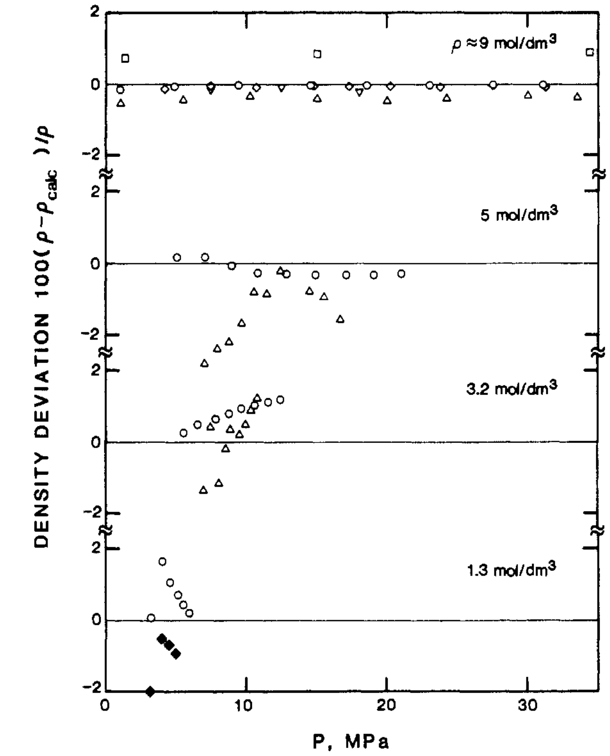

Figure 2. Comparison of *PVT* data for benzene from various sources: ▽, ref *1*; □, ref *2*; ◆, ref *3*; △, ref *4*; ◇, ref *5*; ○, this work. In order to compare data at slightly different densities, we use an equation of state as a base. Absolute deviations from the base line indicate only the ability of the equation to reproduce the data. The relative deviations between data sets indicate the quality of the agreement.

surements. In addition, some samples were held at temperatures of 623 and 723 K for periods in excess of 50 h each while monitoring the pressure. Again, the pressure remained constant within the precision of the measurements. Since no observable effect on the obtained pressures was detected, even above 650 K where decomposition was confirmed, the last measurements were routinely made to the maximum temperature of 723 K.

The data from the present work are tabulated in Table I. In order to allow a convenient comparison with data from other sources at slightly different temperatures and pressures we use an equation of state for benzene, due to Goodwin (*7*), as a base line. Comparisons with various data sets which overlap with the present work are shown in Figure 2. The data of Gehrig and Lentz (*4*) along isochores cover the widest range; however, comparison with these data over the complete range is complicated by the fact that their densities for adjacent isochores appear to be irregular (*7*). The data of Teichmann (*5*) along isochores and of Glanville and Sage (*2*) and Connolly and Kandalic (*1*) along isotherms are confined primarily to the higher density region below the critical temperature. Comparison with these data sets at approximately 9 mol/dm^3 is shown at the top of Figure 2. Agreement with the results of ref *1*, *4*, and *5* is excellent; however, the data of ref *2* appear to be somewhat high. At lower densities and higher temperatures the differences between our data and those of ref *4* often exceed 3-4% and the isochores exhibit dissimilar trends as indicated in the second and third plots of Figure 2. This discrepancy is well outside of our estimated experimental uncertainty of 0.5% in density and is inconsistent with the accuracy we have reported for other fluids (*6*, *8*). Comparison with the data of Gornowski et al. (*3*) is confined to low pressures and lower densities because of the limited range of their data. A comparison with the data of ref *3* at approximately 1.3 mol/dm^3 is shown in the lower plot in Figure 2. Absolute density deviations from the base line shown in Figure 2 reflect only the ability of the equation of state to reproduce the data; it is the relative difference between the data sets that indicates the quality of the agreement.

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Solubilities of Synthesis Gas Components in a Paraffinic Oil under Methanol Synthesis Conditions

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The solubilities of synthesis gas components hydrogen, carbon monoxide, carbon dioxide, and nitrogen in a paraffinic oil were measured at the operating conditions of methanol synthesis in the slurry phase. Gas solubilities were expressed by Henry's constants. The effect of temperature on gas solubilities was correlated with the molar heats of absorption. The results are useful for analysis of reaction kinetics and for modeling of methanol synthesis and other processes of syngas conversion in the slurry phase.

Introduction

An increasing activity in research and development of methanol synthesis in the liquid phase (*1*-*6*) has been recently observed. The novel feature of this technology is that methanol is derived from the conversion of synthesis gas over a catalyst dispersed in an inert liquid. Usually a paraffinic base mineral oil, e.g., Freezene-100 oil (*2*, *3*), or molten paraffin wax (Vestowax SH 105) (*5*, *6*) are used as the nonvolatile liquid medium. The selection of suitable liquid being simultaneously a catalyst carrier and heat-transfer medium is of great importance.

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