Volumetric and Phase Behavior of Propane-Benzene System

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The specific volume of mixtures of propane and benzene was determined at pressures from approximately 100 to 10,000 pounds per square inch absolute at seven temperatures between 40° and 460° F. The composition of the dew-point gas was measured at five temperatures between 10° and 460° F. for pressures between the vapor pressure of benzene and the critical pressure of the system. The results are presented in tabular form, with a limited number of illustrative diagrams.

THE volumetric behavior of propane has been investigated in some detail (*1, 4, 9*) and the critical state has been well established (*2*). Recently (*7*) the volume of this hydrocarbon was measured at pressures up to 10,000 pounds per square inch (all pressures reported in pounds per square inch, absolute) in the temperature interval between 100° and 460° F. and good agreement between these recent measurements and earlier data was obtained. It is believed that the volumetric characteristics of this hydrocarbon are sufficiently well known for most industrial purposes within this temperature interval.

Benzene has also been the subject of relatively extensive experimental investigation. Its volume as a function of pressure has been studied over several different ranges of pressure and temperature (*5, 6, 10*). Satisfactory agreement was obtained among the several sets of volumetric data, including information relating to the vapor pressure of this compound, and it appears that within the temperature range from 100° and 460° F. the volumetric behavior of this compound is well established for pressures up to 10,000 pounds per square inch. No phase equilibrium or volumetric data concerning the behavior of mixtures of propane and benzene appear to be available in the range of conditions of industrial interest.

METHODS AND EQUIPMENT

The equipment employed in this study has already been described (*8*). In principle the procedure involved the introduction of known weights of propane and benzene into a stainless steel vessel whose effective volume was modified by the introduction or withdrawal of mercury. Equilibrium was obtained by the use of mechanical agitation and the temperature was controlled by immersing the vessel in an agitated oil bath. The temperature relative to the International Platinum Scale was determined from the indications of a strain-free platinum resistance thermometer which was compared with the indications of a similar instrument calibrated at the National Bureau of Standards. The pressure within the vessel was measured by means of a balance (*8*) which was calibrated against the vapor pressure of carbon dioxide (*3*) at the ice point as a standard. The variation in the calibration of this instrument in a decade was less than 0.04%. The temperature of measurement was known within 0.03° F. relative to the International Platinum Scale. The effective volume of the working cell was established with an uncertainty of 0.1% at the minimum total volume of the apparatus. The average uncertainty in this variable was considered to be 0.04%. The samples of propane and benzene were added by the use of weighing bombs (*8*) with an uncertainty of 0.02%. From the foregoing data it is estimated that the probable uncertainty in the reported values of the molal volume was 0.25%. The composition of the gas phase, coexisting with liquid, was determined by withdrawing samples from the above-described equipment under isobaric-isothermal conditions. The compositions of the samples withdrawn were established by gas density measurements.

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MATERIALS

The propane employed in this study was obtained from the Phillips Petroleum Company and was reported to contain less than 0.001 mole fraction impurities. This material was subjected to fractionation in a glass column packed with helices. The initial and final tenths of the overhead were discarded in the course of a fractionation carried out at a reflux ratio of approximately 50. The purified hydrocarbon was stored in a steel weighing bomb (*8*). It was found that at 100° F. a change in quality (fraction of the sample in the gas phase) from 0.03 to 0.5 resulted in a change in the two-phase pressure of less than 0.2 pound per square inch. In addition, the value of the vapor pressure at 280° F. agreed closely with recently published data (*7*).

The benzene was purchased as the chemically pure grade and

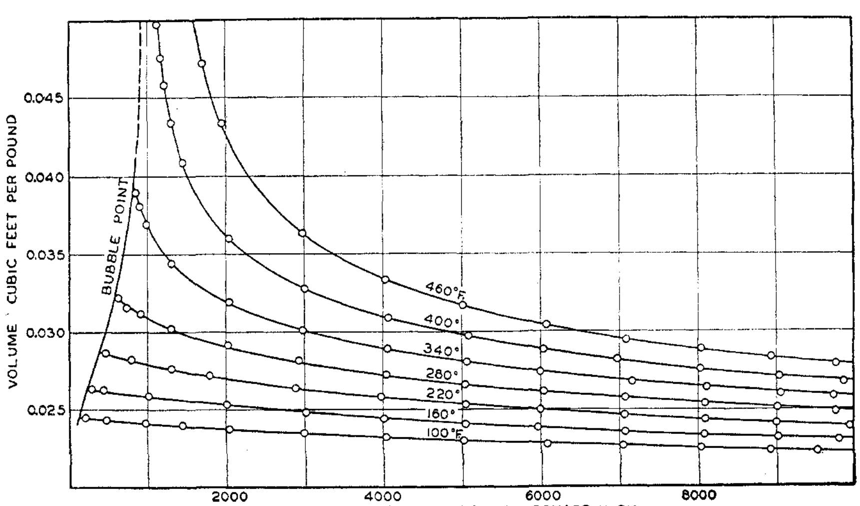

Figure 1. Specific Volume of Mixture Containing 0.4507 Weight Fraction Propane

Table I. Volumetric Behavior of Propane-Benzene System

Pressure, Lb./Sq. In. Abs.	Weight Fraction Propane 0.1207 Z^a	0.1207 V^a	0.2692 Z	0.2692 V	0.4507 Z	0.4507 V	0.8095 Z	0.8095 V
				100° F.				
Dew point	...	...	...	...	...	...	...	...
Bubble point	0.01456 (60.6)[b]	0.02020	0.02231 (94.4)	0.02195	0.02896 (122.1)	0.02458	0.04019 (165.4)	0.03035
80	0.01922	0.02020	...	...	...	...	...	...
100	0.02402	0.02019	0.02364	0.02195	...	...	...	...
125	0.03002	0.02019	0.02959	0.02194	0.02964	0.02457	...	...
150	0.03601	0.02018	0.03542	0.02193	0.03553	0.02455	...	...
200	0.04799	0.02017	0.04721	0.02192	0.04734	0.02453	0.04855	0.03032
300	0.07195	0.02016	0.07072	0.02189	0.07089	0.02449	0.07258	0.03022
400	0.09584	0.02014	0.09421	0.02187	0.09433	0.02444	0.09645	0.03012
500	0.1197	0.02012	0.1176	0.02184	0.1177	0.02439	0.12017	0.03002
600	0.1435	0.02010	0.1410	0.02182	0.1409	0.02434	0.14372	0.02992
800	0.1910	0.02007	0.1876	0.02177	0.1872	0.02425	0.19041	0.02973
1000	0.2384	0.02004	0.2339	0.02172	0.2332	0.02417	0.2366	0.02955
1250	0.2973	0.01999	0.2914	0.02165	0.2903	0.02406	0.2937	0.02935
1500	0.3558	0.01994	0.3488	0.02159	0.3468	0.02396	0.3502	0.02916
1750	0.4143	0.01990	0.4057	0.02153	0.4031	0.02387	0.4060	0.02898
2000	0.4725	0.01986	0.4624	0.02147	0.4589	0.02378	0.4615	0.02882
2250	0.5305	0.01982	0.5188	0.02141	0.5145	0.02370	0.5163	0.02866
2500	0.5880	0.01977	0.5748	0.02135	0.5697	0.02362	0.5706	0.02851
2750	0.6455	0.01973	0.6298	0.02129	0.6248	0.02355	0.6246	0.02837
3000	0.7027	0.01969	0.6862	0.02124	0.6796	0.02348	0.6780	0.02823
3500	0.8169	0.01962	0.7972	0.02115	0.7884	0.02335	0.7840	0.02798
4000	0.9298	0.01954	0.9072	0.02106	0.8964	0.02322	0.8893	0.02777
4500	1.0423	0.01947	1.0162	0.02097	1.0031	0.02310	0.9932	0.02757
5000	1.1539	0.01940	1.1248	0.02089	1.1098	0.02300	1.0972	0.02741
6000	1.3754	0.01927	1.3401	0.02074	1.3205	0.02281	1.3013	0.02709
7000	1.5930	0.01913	1.5526	0.02061	1.5290	0.02264	1.5002	0.02677
8000	1.8082	0.01900	1.7661	0.02050	1.7342	0.02247	1.6947	0.02646
9000	2.0225	0.01889	1.9772	0.02040	1.9361	0.02229	1.8863	0.02618
10,000	2.2389	0.01882	2.1872	0.02031	2.1355	0.02213	2.0735	0.02590
				160° F.				
Dew point	...	...	...	...	...	...	...	...
Bubble point	0.02448 (107.3)[b]	0.02123	0.03946 (174.3)	0.02328	0.05341 (232.4)	0.02637	0.08091 (328.9)	0.03402
125	0.02849	0.02121	...	...	...	...	...	...
150	0.03417	0.02120	...	...	...	...	...	...
200	0.04549	0.02117	0.04526	0.02327	...	...	...	...
300	0.06811	0.02113	0.06781	0.02324	0.06886	0.02634	...	...
400	0.09064	0.02109	0.09025	0.02320	0.09158	0.02627	0.09790	0.03385
500	0.1131	0.02105	0.1126	0.02316	0.1141	0.02620	0.12148	0.03360
600	0.1355	0.02102	0.1349	0.02312	0.1367	0.02614	0.14473	0.03336
800	0.1801	0.02095	0.1793	0.02304	0.1813	0.02601	0.19043	0.03292
1000	0.2243	0.02088	0.2234	0.02297	0.2255	0.02588	0.2351	0.03252
1250	0.2795	0.02081	0.2780	0.02287	0.2803	0.02573	0.2899	0.03208
1500	0.3343	0.02074	0.3323	0.02278	0.3345	0.02559	0.3439	0.03171
1750	0.3888	0.02068	0.3864	0.02270	0.3882	0.02545	0.3972	0.03139
2000	0.4433	0.02063	0.4400	0.02262	0.4412	0.02532	0.4499	0.03111
2250	0.4975	0.02058	0.4930	0.02253	0.4939	0.02519	0.5021	0.03086
2500	0.5515	0.02053	0.5459	0.02245	0.5459	0.02506	0.5537	0.03063
2750	0.6054	0.02049	0.5983	0.02237	0.5978	0.02494	0.6049	0.03042
3000	0.6592	0.02045	0.6507	0.02230	0.6492	0.02483	0.6555	0.03022
3500	0.7657	0.02036	0.7543	0.02216	0.7510	0.02462	0.7554	0.02985
4000	0.8712	0.02027	0.8566	0.02202	0.8516	0.02443	0.8532	0.02950
4500	0.9757	0.02018	0.9589	0.02191	0.9509	0.02425	0.9495	0.02918
5000	1.0793	0.02009	1.0601	0.02180	1.0495	0.02408	1.0456	0.02892
6000	1.2855	0.01994	1.2593	0.02158	1.2451	0.02381	1.2347	0.02846
7000	1.4884	0.01979	1.4576	0.02141	1.4378	0.02357	1.4208	0.02807
8000	1.6916	0.01968	1.6534	0.02125	1.6270	0.02334	1.6023	0.02770
9000	1.8924	0.01957	1.8469	0.02110	1.8137	0.02312	1.7798	0.02735
10,000	2.0898	0.01945	2.0385	0.02096	1.9986	0.02293	1.9530	0.02701
				220° F.				
Dew point	...	...	...	...	...	...	...	...
Bubble point	0.03772 (172.6)[b]	0.02231	0.06238 (282.3)	0.02492	0.08950 (392.0)	0.02874	0.1565 (571.8)	0.04152
200	0.04368	0.02230	...	...	...	...	...	...
300	0.06541	0.02226	0.06624	0.02490	...	...	...	...
400	0.08705	0.02222	0.08803	0.02482	0.09129	0.02873	...	...
500	0.1086	0.02218	0.1097	0.02474	0.1135	0.02858	...	...
600	0.1301	0.02214	0.1312	0.02466	0.1357	0.02845	0.1623	0.04103
800	0.1729	0.02206	0.1739	0.02452	0.1793	0.02820	0.2044	0.03876
1000	0.2153	0.02198	0.2163	0.02439	0.2222	0.02797	0.4262	0.03734
1250	0.2680	0.02189	0.2687	0.02424	0.2751	0.02769	0.2986	0.03623
1500	0.3203	0.02180	0.3205	0.02410	0.3270	0.02744	0.3502	0.03540
1750	0.3723	0.02172	0.3719	0.02397	0.3783	0.02721	0.4009	0.03475
2000	0.4237	0.02163	0.4229	0.02385	0.4290	0.02700	0.4508	0.03419
2250	0.4749	0.02155	0.4736	0.02374	0.4792	0.02680	0.5002	0.03372
2500	0.5260	0.02148	0.5238	0.02363	0.5288	0.02662	0.5490	0.03331
2750	0.5767	0.02141	0.5735	0.02352	0.5782	0.02646	0.5970	0.03293
3000	0.6270	0.02134	0.6230	0.02342	0.6268	0.02630	0.6447	0.03260
3500	0.7274	0.02122	0.7206	0.02322	0.7234	0.02602	0.7381	0.03199
4000	0.8266	0.02110	0.8175	0.02305	0.8188	0.02576	0.8299	0.03147
4500	0.9256	0.02100	0.9133	0.02289	0.9128	0.02553	0.9202	0.03102
5000	1.0235	0.02090	1.0082	0.02274	1.0062	0.02533	1.0096	0.03063
6000	1.2176	0.02072	1.1954	0.02247	1.1900	0.02496	1.1854	0.02997
7000	1.4069	0.02052	1.3810	0.02225	1.3693	0.02462	1.3576	0.02942
8000	1.5961	0.02037	1.5634	0.02204	1.5462	0.02433	1.5279	0.02897
9000	1.7833	0.02023	1.7437	0.02185	1.7208	0.02406	1.6951	0.02857
10,000	1.9677	0.02009	1.9232	0.02169	1.8943	0.02384	1.8564	0.02816

[a] Z = compressibility factor = PVM/RT; V = specific volume, cubic feet per pound.
[b] Figures in parentheses represent bubble-point or dew-point pressure in pounds per square inch absolute.

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Table I. Volumetric Behavior of Propane-Benzene System (*Continued*)

Pressure, Lb./Sq. In. Abs.	Weight Fraction Propane 0.1207		0.2692		0.4507		0.8095	
	Z[a]	V[a]	Z	V	Z	V	Z	V
				280° F.				
Dew point	...	...	0.8732 (113.0)	0.9484	0.8644 (168.5)	0.7026	...	...
Bubble point	0.05636 (263.1)[b]	0.02380	0.09570 (435.8)	0.02695	0.1406 (595.4)	0.03236	...	...
200	...	...	...	...	...	...	0.8937	0.7377
300	0.06419	0.02377	...	...	...	...	0.8368	0.4605
400	0.08536	0.02371	...	...	...	...	0.7742	0.3195
500	0.1064	0.02365	0.1095	0.02688	...	...	0.7058	0.2330
600	0.1274	0.02359	0.1308	0.02676	0.1416	0.03232	0.6248	0.1719
800	0.1691	0.02348	0.1729	0.02653	0.1841	0.03153	0.4064	0.08387
1000	0.2104	0.02337	0.2145	0.02632	0.2258	0.03093	0.3120	0.05151
1250	0.2614	0.02323	0.2655	0.02607	0.2768	0.03033	0.3308	0.04369
1500	0.3119	0.02310	0.3157	0.02583	0.3271	0.02987	0.3798	0.04180
1750	0.3620	0.02298	0.3652	0.02561	0.3768	0.02949	0.4221	0.03982
2000	0.4115	0.02286	0.4138	0.02539	0.4259	0.02917	0.4673	0.03857
2250	0.4607	0.02275	0.4620	0.02520	0.4742	0.02887	0.5124	0.03760
2500	0.5095	0.02264	0.5097	0.02502	0.5217	0.02858	0.6674	0.03681
2750	0.5577	0.02253	0.5573	0.02487	0.5688	0.02833	0.6018	0.03615
3000	0.6057	0.02243	0.6043	0.02472	0.6147	0.02807	0.6460	0.03555
3500	0.7009	0.02225	0.6973	0.02445	0.7062	0.02763	0.7335	0.03460
4000	0.7946	0.02207	0.7894	0.02422	0.7958	0.02725	0.8185	0.03378
4500	0.8878	0.02192	0.8807	0.02402	0.8843	0.02692	0.9039	0.03316
5000	0.9797	0.02177	0.9708	0.02383	0.9719	0.02662	0.9864	0.03257
6000	1.1611	0.02150	1.1484	0.02349	1.1459	0.02616	1.1485	0.03160
7000	1.3401	0.02127	1.3215	0.02317	1.3151	0.02573	1.3093	0.03088
8000	1.5172	0.02107	1.4921	0.02289	1.4817	0.02537	1.4693	0.03032
9000	1.6939	0.02091	1.6602	0.02264	1.6457	0.02504	1.6262	0.02983
10,000	1.8677	0.02075	1.8268	0.02242	1.8071	0.02475	1.7784	0.02936
				340° F.				
Dew point	...	...	0.8079 (223.1)	0.4805	0.7777 (345.8)	0.3330	...	...
Bubble point	0.08226 (383.7)[b]	0.02575	0.1396 (615.2)	0.03010	0.2200 (823.2)	0.03956	...	...
200	...	...	...	...	...	...	0.8987	0.8020
300	...	...	...	...	...	...	0.8783	0.5225
400	0.08555	0.02569	...	...	...	...	0.8364	0.3732
500	0.1064	0.02556	...	...	...	...	0.7902	0.2821
600	0.1270	0.02542	...	...	...	...	0.7452	0.2217
800	0.1676	0.02517	0.1780	0.02953	...	...	0.6455	0.1440
1000	0.2077	0.02495	0.2186	0.02901	0.2493	0.03691	0.5455	0.09736
1250	0.2574	0.02473	0.2683	0.02848	0.2940	0.03483	0.4683	0.06687
1500	0.3063	0.02453	0.3170	0.02804	0.3406	0.03362	0.4575	0.05444
1750	0.3548	0.02435	0.3648	0.02766	0.3870	0.03274	0.4758	0.04853
2000	0.4030	0.02420	0.4118	0.02732	0.4313	0.03203	0.5087	0.04540
2250	0.4505	0.02405	0.4582	0.02702	0.4782	0.03147	0.5460	0.04331
2500	0.4975	0.02390	0.5042	0.02676	0.5227	0.03096	0.5839	0.04169
2750	0.5440	0.02376	0.5496	0.02652	0.5668	0.03051	0.6232	0.04045
3000	0.5900	0.02362	0.5944	0.02629	0.6105	0.03013	0.6628	0.03943
3500	0.6810	0.02337	0.6829	0.02589	0.6971	0.02949	0.7417	0.03782
4000	0.7703	0.02313	0.7705	0.02556	0.7826	0.02900	0.8203	0.03660
4500	0.8587	0.02292	0.8570	0.02527	0.8663	0.02850	0.8976	0.03560
5000	0.9458	0.02272	0.9428	0.02502	0.9492	0.02811	0.9746	0.03479
6000	1.1175	0.02237	1.1106	0.02456	1.1120	0.02744	1.1258	0.03349
7000	1.2868	0.02207	1.2740	0.02415	1.2706	0.02688	1.2739	0.03248
8000	1.4520	0.02180	1.4355	0.02381	1.4269	0.02641	1.4213	0.03171
9000	1.6185	0.02160	1.5939	0.02350	1.5814	0.02612	1.5687	0.03111
10,000	1.7825	0.02141	1.7477	0.02319	1.7379	0.02573	1.7145	0.03060
				400° F.				
Dew point	...	...	0.7128 (410.3)	0.2478	...	...	...	...
Bubble point	0.1185 (536.6)[b]	0.02852	0.2055 (814.3)	0.03600	...	...	...	...
200	...	...	...	...	0.9018	0.7282	0.9342	0.8962
300	...	...	...	...	0.8636	0.4582	0.9048	0.5787
400	...	...	...	...	0.8084	0.3217	0.8740	0.4192
500	...	...	...	...	0.7478	0.2380	0.8422	0.3232
600	0.1316	0.02831	...	...	0.6790	0.1802	0.8113	0.2594
800	0.1721	0.02777	...	...	0.5078	0.1010	0.7468	0.1791
1000	0.2114	0.02730	0.2366	0.03375	0.3808	0.06062	0.6860	0.1316
1250	0.2598	0.02684	0.2827	0.03226	0.3531	0.04524	0.6228	0.09560
1500	0.3073	0.02645	0.3288	0.03127	0.3788	0.04019	0.5838	0.07468
1750	0.3540	0.02612	0.3742	0.03050	0.4155	0.03779	0.5722	0.06274
2000	0.3999	0.02582	0.4192	0.02990	0.4557	0.03627	0.5804	0.05568
2250	0.4454	0.02556	0.4636	0.02939	0.4963	0.03512	0.6011	0.05126
2500	0.4904	0.02533	0.5077	0.02897	0.5370	0.03420	0.6278	0.04818
2750	0.5350	0.02512	0.5510	0.02858	0.5777	0.03344	0.6584	0.04594
3000	0.5790	0.02492	0.5939	0.02824	0.6182	0.03280	0.6917	0.04424
3500	0.6666	0.02459	0.6785	0.02765	0.6988	0.03178	0.7559	0.04144
4000	0.7528	0.02430	0.7616	0.02716	0.7787	0.03099	0.8256	0.03960
4500	0.8371	0.02402	0.8442	0.02676	0.8575	0.03033	0.8976	0.03827
5000	0.9197	0.02375	0.9251	0.02639	0.9554	0.02978	0.9725	0.03732
6000	1.0818	0.02328	1.0840	0.02577	1.0893	0.02890	1.1139	0.03562
7000	1.2415	0.02290	1.2382	0.02523	1.2406	0.02821	1.2503	0.03427
8000	1.3990	0.02258	1.3904	0.02479	1.3873	0.02760	1.3880	0.03329
9000	1.5558	0.02232	1.5402	0.02441	1.5320	0.02710	1.5249	0.03251
10,000	1.7100	0.02208	1.6868	0.02406	1.6781	0.02671	1.6615	0.03188

(*Concluded on page 511*)

Table I. Volumetric Behavior of Propane-Benzene System (*Concluded*)

Pressure, Lb./Sq. In. Abs.	Weight Fraction Propane 0.1207 Z^a	0.1207 V^a	0.2692 Z	0.2692 V	0.4507 Z	0.4507 V	0.8095 Z	0.8095 V
	460° F.							
Dew point	...	...	...	...	...	...	...	...
Bubble point	0.1758(720.8)[b]	0.03369	...	...	...	...	...	...
200	...	...	0.9039	0.6896	0.9332	0.7946	0.9498	0.9747
300	...	...	0.8528	0.4338	0.8937	0.5073	0.9255	0.6332
400	...	...	0.7960	0.3037	0.8560	0.3644	0.9021	0.4629
500	...	...	0.7330	0.2237	0.8137	0.2771	0.8780	0.3604
600	...	...	0.6636	0.1688	0.7695	0.2184	0.8540	0.2921
800	0.1889	0.03262	0.4820	0.09194	0.6757	0.1439	0.8062	0.2068
1000	0.2250	0.03108	0.3395	0.05180	0.5821	0.09912	0.7651	0.1570
1250	0.2715	0.03000	0.3300	0.04028	0.4939	0.06729	0.7220	0.1186
1500	0.3172	0.02921	0.3612	0.03674	0.4690	0.05325	0.6885	0.09421
1750	0.3621	0.02858	0.3990	0.03479	0.4789	0.04660	0.6700	0.07858
2000	0.4063	0.02806	0.4390	0.03349	0.5020	0.04275	0.6655	0.06830
2250	0.4499	0.02762	0.4788	0.03247	0.5334	0.04037	0.6718	0.06128
2500	0.4928	0.02723	0.5185	0.03165	0.5694	0.03879	0.6868	0.05639
2750	0.5351	0.02688	0.5595	0.03105	0.6042	0.03744	0.7081	0.05285
3000	0.5771	0.02657	0.6002	0.03053	0.6395	0.03630	0.7333	0.05017
3500	0.6601	0.02605	0.6796	0.02963	0.7121	0.03465	0.7905	0.04636
4000	0.7419	0.02562	0.7584	0.02893	0.7866	0.03349	0.8522	0.04378
4500	0.8226	0.02525	0.8361	0.02835	0.8588	0.03250	0.9153	0.04175
5000	0.9020	0.02492	0.9126	0.02785	0.9307	0.03170	0.9798	0.04022
6000	1.0506	0.02437	1.0632	0.02704	1.0726	0.03044	1.1091	0.03794
7000	1.2112	0.02390	1.2093	0.02636	1.2145	0.02954	1.2363	0.03625
8000	1.3593	0.02347	1.3511	0.02577	1.2547	0.02887	1.3642	0.03500
9000	1.5058	0.02311	1.4922	0.02530	1.4962	0.02831	1.4917	0.03402
10,000	1.6484	0.02277	1.6318	0.02490	1.6316	0.02778	1.6175	0.03320

[a] Z = compressibility factor = PVM/RT; V = specific volume, cubic feet per pound.
[b] Figures in parentheses represent bubble-point or dew-point pressure in pounds per square inch absolute.

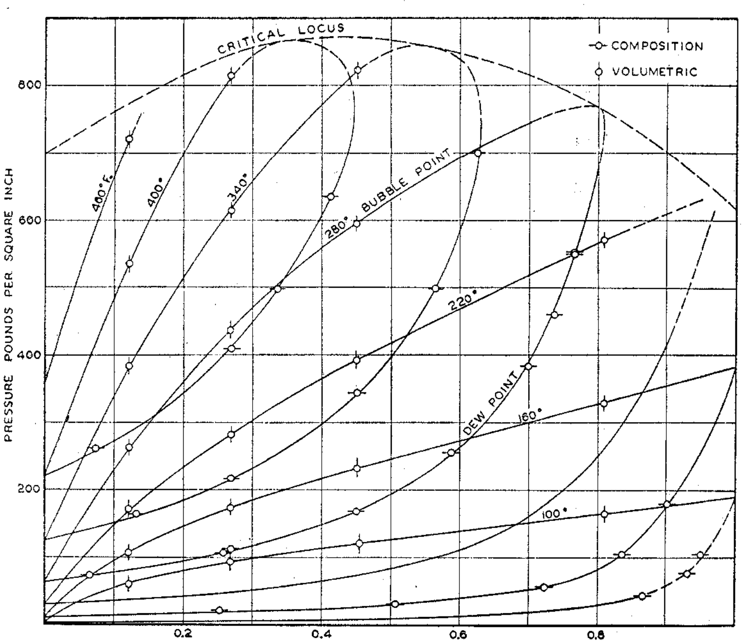

Figure 2. Pressure-Composition Diagram of Propane-Benzene System

was subjected to three sequential partial crystallizations. The initial and final tenths of the material to melt or crystallize were discarded in each case. The purified material was fractionated in a 30-plate glass column at a relatively low pressure. The initial and final eighths of the overhead were discarded. The index of refraction of the purified material as determined at 77° F. for the D-lines of sodium was 1.503. The specific volume at 100° F. and atmospheric pressure was 0.1861 cubic foot per pound. The material was stored in a steel weighing bomb until ready for use.

EXPERIMENTAL RESULTS

The influence of pressure and temperature upon the specific volume of four mixtures of propane and benzene was determined at seven temperatures between 100° and 460° F. These measurements were extended to a maximum pressure of 10,000 pounds per square inch. Table I records the specific volume of the four mixtures in the single-phase region. The data have been smoothed to even values of pressure for the temperatures studied experimentally.

The values of bubble-point pressure were obtained from discontinuity in the first derivative of the specific volume with respect to pressure. Figure 1 shows the specific volume of a mixture containing 0.4507 weight fraction propane. The density of the experimental points is typical of all of the data obtained. The curves were based upon the smoothed data and it was found that the average deviation of the individual experimental measurements from the smoothed data was less than 0.05%.

In Table II are recorded values of the ratio of the experimentally determined specific volume to that predicted on the basis of additive volumes of the components (*6, 7*). The deviation from additive volumes is somewhat larger than is experienced in the case of mixtures of aliphatic hydrocarbons.

The composition of the dew-point gas was determined at a series of pressures for five temperatures. The results of these

Table II. Ratio of Actual to Ideal Volume of Mixtures of Propane and Benzene

Pressure, Lb./Sq. In. Abs.	Weight Fraction Propane 0.1207	0.2692	0.4507	0.8095
	100° F.			
2000	0.9950	0.9790	0.9770	0.9907
4000	0.9990	0.9864	0.9868	0.9968
10,000	1.0000	0.9985	0.9968	1.0012
	220° F.			
2000	0.9792	0.9578	0.9531	0.9738
4000	0.9920	0.9796	0.9795	0.9906
10,000	1.0055	0.9982	0.9983	1.0018
	340° F.			
2000	0.9294	0.8919	0.8732	0.9405
4000	0.9880	0.9689	0.9660	0.9836
10,000	1.0028	1.1407	0.9988	1.0016

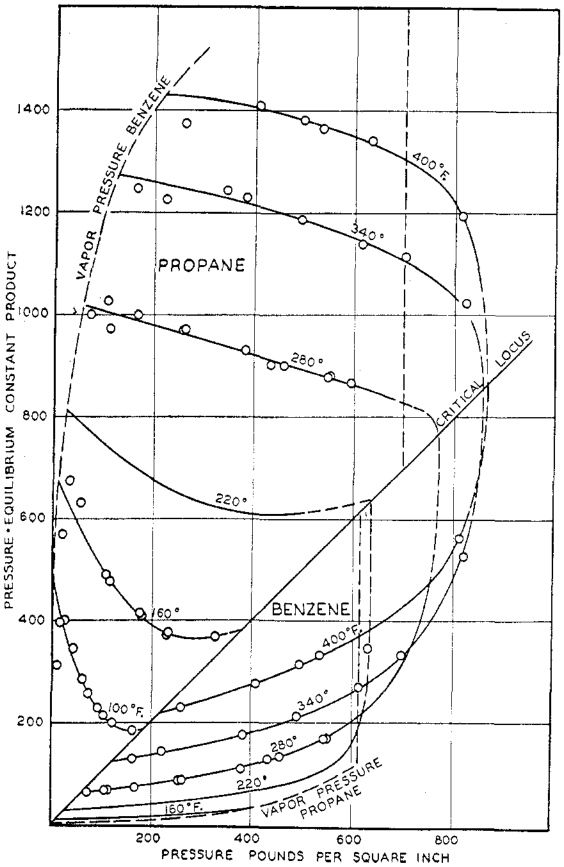

Figure 3. Gas-Liquid Equilibrium Constants for Propane and Benzene

measurements are recorded as a pressure-composition diagram in Figure 2. The experimental points shown were those obtained from the directly measured compositions of the gas phase and from the bubble-point states determined from the volumetric data. Table III presents the compositions of the coexisting phases, together with values of the equilibrium constants for both components. Figure 3 portrays the behavior of the system in terms of the product of pressure and the equilibrium constant for each component. The deviation from Raoult's law at the lower temperatures is complex in that this product for propane exhibits minima at 100°, 160°, and 220° F. The behavior under these conditions does not resemble that found for mixtures of the paraffin hydrocarbons. At the higher temperatures the relation between equilibrium constant and pressure is similar to that found in binary hydrocarbon systems.

The presentation of the data for the equilibrium constant of benzene at temperatures below 280° F. is inadequate in Figure 3. In order to show this region in somewhat greater detail, the ratio of the actual equilibrium constant to the equilibrium constant established from Raoult's law has been depicted as a function of pressure in Figure 4. The relationship of this ratio to other variables is described by the following equation:

$$\frac{K}{K_R} = \frac{YP}{XP''} \tag{1}$$

In this equation, K is the gas-liquid equilibrium constant for the component under consideration, K_R is its equilibrium constant as predicted by Raoult's law, Y and X are the mole fractions of the component in the gas and liquid phases, respectively, P is the pressure, and P'' is the vapor pressure of the pure component.

The precision of determination of the relatively small mole fraction of benzene in the gas phase at 100° F. was not great and

TABLE III. PHASE COMPOSITIONS IN PROPANE-BENZENE SYSTEM

Pressure, Lb./Sq. In. Abs.	Weight Fraction Propane		Equilibrium Constant	
	Gas	Liquid	Propane	Benzene
		100° F.		
3.2[a]	0.0000	0.0000	149.7	1.0000
20	0.7378	0.0228	20.70	0.1741
40	0.8490	0.0624	8.525	0.1021
60	0.9000	0.1194	4.808	0.0734
80	0.9310	0.1980	3.128	0.0579
100	0.9505	0.3038	2.213	0.0506
150	0.9831	0.6801	1.250	0.0445
188.7[b]	1.0000	1.0000	1.000	0.0417
		160° F.		
11.1[a]	0.0000	0.0000	60.99	1.0000
20	0.3046	0.0076	32.85	0.5700
40	0.6114	0.0277	15.30	0.6780
60	0.7420	0.0495	9.892	0.1792
80	0.7980	0.0772	6.783	0.1435
100	0.8280	0.1083	5.038	0.1315
150	0.8780	0.2107	2.889	0.1071
200	0.9172	0.3453	1.970	0.0938
250	0.9481	0.5146	1.488	0.0854
300	0.9727	0.7023	1.220	0.0818
350	0.9903	0.8801	1.071	0.0816
383.8[b]	1.0000	1.0000	1.000	0.0824
		220° F.[c]		
29.2[a]	0.0000	0.0000	27.77	1.0000
40	0.1670	0.0074	20.00	0.7482
60	0.3596	0.0220	13.02	0.5217
80	0.4772	0.0376	9.550	0.4088
100	0.5573	0.0537	7.480	0.3413
150	0.6792	0.1015	4.733	0.2529
200	0.7507	0.1572	3.390	0.2502
250	0.7997	0.2227	2.602	0.1869
300	0.8371	0.2945	2.120	0.1740
350	0.8642	0.3749	1.783	0.1692
400	0.8920	0.4640	1.546	0.1702
450	0.9144	0.5671	1.359	0.1751
500	0.9313	0.6675	1.230	0.1820
550	0.9467	0.7657	1.137	0.2309
600	0.9622	0.8797	1.054	0.3650
639[d]	0.974	0.974	1.000	1.0000
		280° F.		
64.7[a]	0.0000	0.0000	15.70	1.0000
80	0.1108	0.0081	12.64	0.8314
100	0.2206	0.0190	10.06	0.6884
150	0.3992	0.0479	6.610	0.4999
200	0.5077	0.0792	4.888	0.4076
250	0.5819	0.1133	3.854	0.3540
300	0.6352	0.1503	3.165	0.3213
350	0.6750	0.1906	2.671	0.3028
400	0.7047	0.2340	2.304	0.2949
450	0.7255	0.2768	2.039	0.2956
500	0.7474	0.3292	1.788	0.3020
550	0.7645	0.3917	1.599	0.3164
600	0.7814	0.4574	1.442	0.3400
650	0.7991	0.5261	1.308	0.3754
700	0.8052	0.6113	1.194	0.4571
750	0.8084	0.7104	1.085	0.5960
769[d]	0.798	0.798	1.000	1.0000
		340° F.		
126[a]	0.0000	0.0000	10.08	0.1000
150	0.0923	0.0103	8.433	0.8627
200	0.2332	0.0323	6.275	0.6880
250	0.3304	0.0552	4.978	0.5887
300	0.4030	0.0793	4.113	0.5250
350	0.4588	0.1048	3.496	0.4828
400	0.5022	0.1312	3.039	0.4552
450	0.5362	0.1600	2.664	0.4388
500	0.5650	0.1905	2.369	0.4292
550	0.5848	0.2234	2.115	0.4282
600	0.6042	0.2576	1.918	0.4350
650	0.6185	0.2917	1.741	0.4500
700	0.6266	0.3358	1.584	0.4771
750	0.6278	0.3794	1.441	0.5222
800	0.6227	0.4290	1.298	0.5988
850	0.5773	0.4968	1.112	0.8047
859[d]	0.549	0.549	1.000	1.0000
		400° F.		
222.1[a]	0.0000	0.0000	6.430	1.0000
250	0.0571	0.0097	5.702	0.9188
300	0.1456	0.0283	4.733	0.8077
350	0.2059	0.0450	4.036	0.7361
400	0.2588	0.0691	3.506	0.6869
450	0.3062	0.0866	3.090	0.6540
500	0.3384	0.1053	2.756	0.6339
550	0.3685	0.1265	2.482	0.6182
600	0.3944	0.1500	2.250	0.6092
650	0.4184	0.1754	2.047	0.6062
700	0.4366	0.2027	1.866	0.6110
750	0.4461	0.2308	1.696	0.6300
800	0.4419	0.2597	1.523	0.6750
850	0.4132	0.3038	1.273	0.8047
867[d]	0.349	0.349	1.000	1.0000

[a] Vapor pressure of benzene.
[b] Vapor pressure of propane.
[c] All values at 220° F. were interpolated.
[d] Estimated critical states.

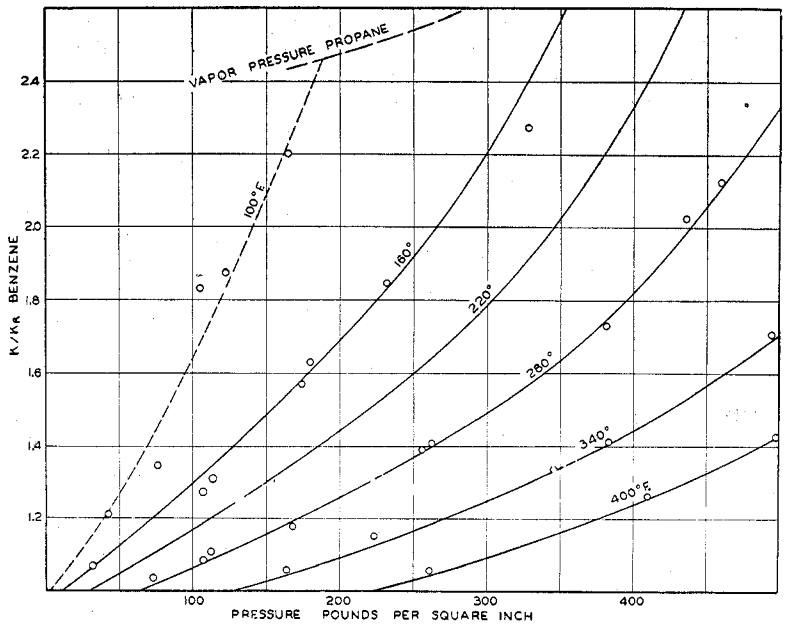

Figure 4. Ratio of Actual to Raoult's Law Equilibrium Constant for Benzene

the corresponding curve in Figure 4 is dotted for this reason. The ratio of the equilibrium constants approaches unity at the vapor pressure of benzene at each temperature. The greater deviation from Raoult's law in the case of the propane-benzene system than for mixtures of the aliphatic hydrocarbons of comparable volatility is not surprising when the difference in molecular structure of the compounds is considered.

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LITERATURE CITED

(1) Beattie, Kay, and Kaminsky, *J. Am. Chem. Soc.*, 59, 1589 (1937).
(2) Beattie, Poffenberger, and Hadlock, *J. Chem. Phys.*, 3, 96 (1935).
(3) Bridgeman, *J. Am. Chem. Soc.*, 49, 1174 (1927).
(4) Dana, Jenkins, Burdick, and Timm, *Refrig. Eng.*, 12, 387 (1926).
(5) Gibson and Kincaid, *J. Am. Chem. Soc.*, 60, 511 (1938).
(6) Glanville and Sage, Ind. Eng. Chem., 41, 1272 (1949).
(7) Reamer, Sage, and Lacey, *Ibid.*, 41, 482 (1949).
(8) Sage and Lacey, *Trans. Am. Inst. Mining Met. Engrs.*, 136, 136 (1940).
(9) Sage, Schaafsma, and Lacey, Ind. Eng. Chem., 26, 1218 (1934).
(10) Young, *Sci. Proc. Roy. Dublin Soc.*, 12, 374 (1910).

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Reaction of Iron with Organic Sulfur Compounds

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A BETTER knowledge of the reaction of organic sulfur compounds with iron and other common metals is of interest, particularly in the fields of corrosion and extreme pressure lubrication. Crude petroleum oils contain large amounts of sulfur in various forms and corrosion of equipment through chemical attack by the sulfur is encountered at various stages of processing. Low temperature corrosion from sulfur in reduced forms (at below 100° C.) is generally associated with free sulfur, hydrogen sulfide, or polysulfides. This problem has been discussed in the literature on pipe-line corrosion and its prevention, and in many reports on corrosion by sulfur, sulfides, and hydrogen sulfide.

Corrosion by organic sulfur compounds or by decomposition products of organic sulfur compounds becomes more important in processing operations wherein the sulfur-containing petroleum is in contact with metals at temperatures above 100° C. When petroleum is cracked at temperatures of 400° to 500° C. and higher, a large portion of the sulfur is eliminated as hydrogen

In the temperature range 125° to 275° C., many organic compounds containing bivalent sulfur react with iron. In this reaction a major portion of the sulfur is transferred to the iron as a material which is insoluble in organic liquids and appears to be principally ferrous sulfide. This reaction is common both to corrosion problems in this temperature range and to the action of sulfur compounds as extreme pressure lubricant additives, a problem in controlled corrosion. The extent of the reactions of sulfurized terpene hydrocarbons, sulfurized sperm oil, and *n*-dodecyl mercaptan with iron is compared over the temperature range 100° to 275° C., and an attempt is made to establish a sulfur balance throughout the range. Experiments on the reaction of copper with several sulfur compounds are reported. A division of sulfur compounds into two classes, based on extreme pressure lubricant tests, is made. Within one group the rate of reaction with iron appears to correlate with effectiveness in these tests. Compounds in the second group which appear to react with iron at the same rate are quite ineffective. Two different corrosion processes appear to be involved; both of these terminate in the formation of the same iron sulfide on the iron surface. Chemical differences between the processes are not known but presumably must exist.