conditions the left-hand side of Equation 1 is not equal to zero; instead, the true equality is

$$x_1 \frac{d \ln \gamma_1}{dx_1} + x_2 \frac{d \ln \gamma_2}{dx_1} = \frac{-\Delta H}{RT^2} \frac{dT}{dx_1} \qquad (3)$$

where ΔH is the integral molal heat of mixing at the composition defined by x_1 and x_2. While in many binary systems ΔH and dT/dx are sufficiently small to make Equation 1 a good approximation for Equation 3, one cannot overlook the cases in which the right-hand side of Equation 3 is not negligible—e.g., the case of acetic acid and water (1), although this is complicated by the occurrence of association in the vapor. Thus, the behavior of γ_1 and γ_2 in the present system may be accounted for by assigning appropriate values to ΔH.

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Volumetric and Phase Behavior in the Nitric Acid–Nitrogen Dioxide–Water System

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Pressure-volume-temperature measurements on three mixtures of nitric acid, nitrogen dioxide, and water at physical and chemical equilibrium were made at temperatures between 190° and 340° F. and at pressures up to 5000 pounds/square inch absolute. The ratio of the weight fraction of water to the sum of the weight fractions of water and nitric acid was kept essentially constant.

This restricted ternary system showed a decrease in bubble-point pressure at physicochemical equilibrium with increasing concentration of nitrogen dioxide. The bubble-point pressure reached a minimum at 0.10 weight fraction nitrogen dioxide and gradually became greater at higher weight fractions. At the lower concentrations of nitrogen dioxide, chemical equilibrium at 190° F. was achieved only after several hours elapsed. As the concentration of nitrogen dioxide was increased, the approach to equilibrium was more rapid.

Experimental information is available concerning the volumetric and phase behavior at physical equilibrium of nitric acid and its mixtures with water and nitrogen dioxide. Klemenc and Rupp (6) contributed materially to the knowledge of the volumetric behavior of the liquid phase at atmospheric pressure. Taylor compiled information concerning the bubble-point pressure of mixtures of nitric acid and water (19). The freezing points of the nitric acid-water system were investigated, and at least two hydrates of nitric acid were reported (8). Forsythe and Giauque (4) added greatly to the knowledge of the thermodynamic properties of nitric acid and its mixtures with water. Sprague (17) proposed several analytical expressions for variations in specific weight with composition for the nitric acid-nitrogen dioxide-water system. All of the above studies were made at physical equilibrium only, without regard for the gradual chemical rearrangement which takes place in these systems even at ambient temperature.

Information obtained at both physical and chemical equilibrium for pure nitric acid (11, 15,20), the nitric acid-nitrogen dioxide system (2), the nitric acid-water system (3), and for samples of commercial red and white fuming nitric acid (12) is available. Additional information concerning mixtures of nitric acid, water, and nitrogen dioxide during their approach to physical and chemical equilibrium was obtained (20).

Insufficient experimental information is available to predict the volumetric and phase behavior of ternary mixtures of nitric acid, water, and nitrogen dioxide in the composition interval normally encountered in industrial practice. For this reason an investigation of the specific volume and the bubble-point pressure of three mixtures of nitric acid, water, and nitrogen dioxide was made. All three of the mixtures were selected so as to yield a ratio of the weight fraction of water to the combined weight fractions of nitric acid and water of approximately 0.090. The investigation was carried out at pressures up to 5000 pounds/square inch absolute in the temperature interval between 190° and 340° F. The time required for the attainment of chemical equilibrium at temperatures below 190° F. was great enough to render investigation unprofitable at lower temperatures. All measurements were made at both chemical and physical equilibrium except that limited information is included concerning the approach to chemical equilibrium.

EQUIPMENT AND METHODS

The methods and equipment employed in this investigation were the same as those used (11) for the study of the behavior of pure nitric acid at physical and chemical equilibrium. The sample was confined within a glass piston-cylinder combination (11) which was surrounded by a fluorinated hydrocarbon confined within a stainless steel pressure vessel. Introduction and withdrawal of the fluorinated hydrocarbon accomplished the change in volume of the sample within the glass piston-cylinder combination. Clearances between the piston and cylinder were sufficiently small so that there was very little tendency for loss of the sample into the fluorinated hydrocarbon. Experience with this equipment indicates that the relative probable error in the measurement of specific volume was 0.6% after calibration as a function of pressure and temperature.

The quantity of nitrogen dioxide employed was deter-

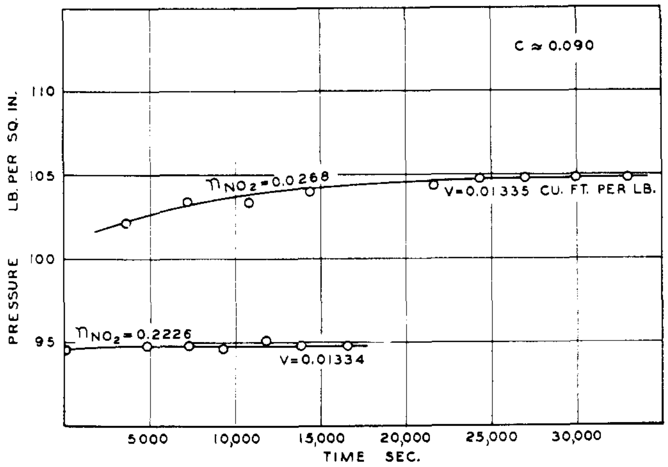

Figure 1. Change in pressure with time under isochoric conditions at 190° F.

mined gravimetrically by weighing-bomb techniques (15). A mixture of nitric acid and water was prepared by gravimetric methods and introduced into the piston-cylinder combination by a volumetric procedure which has been described (11). The quantity of each of the components introduced into the working section was known within 0.2%. Introduction of prepared mixtures of water and nitric acid of known composition permitted measurements to be made at nearly the same ratio of nitric acid to water for all of the mixtures investigated.

Pressures were measured by means of a balance (15) which was calibrated against the vapor pressure of carbon dioxide at the ice point (1). The pressure within the piston-cylinder combination was known within 1.5 pounds/square inch or 0.2%, whichever was the larger uncertainty. Temperatures were determined by means of a strain-free, platinum resistance thermometer of the coil filament type (10). This instrument was calibrated against a similar device which had been submitted to the National Bureau of Standards for certification. Temperatures recorded were related to the international platinum scale within 0.1° F. The primary uncertainty in measurement rested in the attainment of chemical equilibrium in the heterogeneous region. The over-all probable error in specific volume at chemical equilibrium may exceed 2% in the heterogeneous region, assuming negligible errors in pressure, temperature, and composition.

MATERIALS

Nitric acid was prepared from potassium nitrate and sulfuric acid by established methods (4). It was redistilled once at a pressure below 0.005 inch of mercury, and the central portion of the overhead was retained for use. The sample of acid employed had a specific weight of 93.827 pounds/cubic foot at 77° F., that may be compared with 93.873 pounds/cubic foot obtained by Stern and Kay (18) and 93.755 pounds/cubic foot reported by Klemenc and Rupp (6). The specific conductance of nitric acid prepared in the same equipment (4) was 3.77 reciprocal ohm-cm. at 32° F. (13). Experience with nearly pure nitric acid indicates that the sample used in this investigation contained less than 0.001 weight fraction of material other than nitric acid. Distilled water was obtained from the laboratory supply and deaerated by boiling at reduced pressure.

Nitrogen dioxide was supplied from commercial sources and subjected to two sequential fractionations at atmospheric pressure in a column provided with 16 glass plates. The central third of the overhead was collected from each distillation, which was carried out at a reflux ratio of approximately 20. Purified nitrogen dioxide was stored in a stainless steel weighing bomb (15) until ready for use. Throughout this discussion the term nitrogen dioxide is used to describe equilibrium mixtures of nitrogen dioxide and nitrogen tetroxide. Since results are presented upon a weight basis, no uncertainty is introduced by ambiguity as to the molecular species encountered.

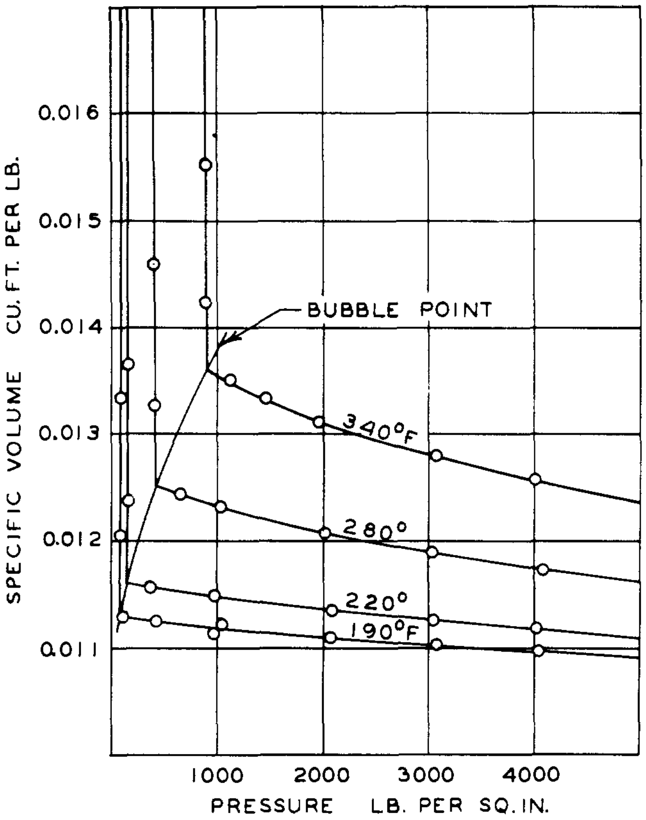

Figure 2. Experimental measurements upon mixture III

APPROACH TO EQUILIBRIUM

The attainment of physical equilibrium within the precision of measurement required approximately 10 minutes after the system was brought to a uniform temperature. The attainment of chemical equilibrium varied markedly depending upon the temperature and the weight fraction of nitrogen dioxide. This behavior follows the trends found in the nitric acid-water (3) and in the nitric acid-nitrogen dioxide (2) systems in that the presence of water decreased the rate of attainment of chemical equilibrium whereas the addition of nitrogen dioxide increased it. At a temperature of 190° F. several hours were required, while at 250° F. the factors influencing the attainment of physical equilibrium became important. Figure 1 shows the approach to chemical equilibrium under isochoric conditions for two of the three mixtures investigated at a temperature of 190° F. These results indicate an increase in rate of attainment of chemical equilibrium with an increase in weight fraction nitrogen dioxide.

EQUILIBRIUM BEHAVIOR

Three mixtures of nitric acid, nitrogen dioxide, and water were investigated. Each of these mixtures was prepared with nearly the same ratio of nitric acid to water.

The characterizing composition parameter was defined as follows:

$$C = \frac{{}^{n}\mathrm{H_2O}}{{}^{n}\mathrm{H_2O} + {}^{n}\mathrm{HNO}} \qquad (1)$$

The compositions of the three mixtures investigated, expressed in weight fraction along with values of the composition parameter C defined by Equation 1, are

	Mixture I	Mixture II	Mixture III
Nitric acid	0.8858	0.8136	0.7075
Water	0.0874	0.0833	0.0699
Nitrogen dioxide	0.0268	0.1031	0.2226
Composition parameter C	0.0898	0.0929	0.0899

For each mixture, the specific volume was determined as a function of pressure for at least three and usually four temperatures in the interval between 190° and 340° F. Pressures up to 5000 pounds/square inch were used.

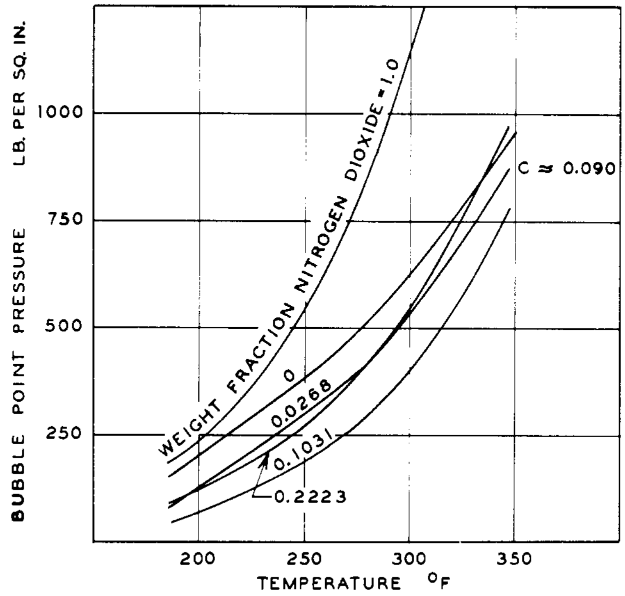

Figure 3. Effect of temperature upon bubble point pressure of experimentally studied mixtures

The results of these measurements upon one of the mixtures are shown in Figure 2 where the curves result from smoothing the data with respect to pressure, temperature, and composition. Throughout the smoothing operations the mixtures were treated as part of a restricted ternary system (14).

Deviations of the experimental specific volumes from the smoothed data for each mixture investigated are comparable to the expected reproducibility of the measurements:

	Mixture I	Mixture II	Mixture III	Average
Average Deviation				
With sign, cu. ft. /lb.	0.000079	0.000094	-0.000002	0.000057
Without sign, cu. ft. /lb.	0.000175	0.000149	0.000007	0.000110
Standard Deviation				
Absolute, cu. ft. /lb.	0.000106	0.000064	0.000011	0.000060
Relative, %	0.87	0.54	0.09	0.50

It should be emphasized that in order to obtain the experimental points shown in Figure 2, several hours were required in order to attain chemical equilibrium at each point. The over-all relative standard deviation of the experimental data from the smoothed curves was 0.50% which is comparable to that found in earlier studies of the nitric acid-water system (3). The data shown in Figure 2 yielded smaller deviations from the smoothed data because of the more rapid attainment of chemical equilibrium as a result of the higher weight fraction of nitrogen dioxide.

Results of the investigation in the single-phase region are recorded as smoothed values of the specific volume in Table I with pressure and temperature as independent variables. In order to show more effectively the results obtained in the heterogeneous region, the values of pressure were recorded as functions of even values of temperature and specific volume in Table II for each of the mixtures.

Bubble-point pressure for each of the three mixtures investigated is depicted as a function of temperature in Figure 3. Behavior of a binary mixture of nitric acid and water (3) corresponding to the same value of the composition parameter C was included on this diagram. In addition the vapor pressure of nitrogen dioxide (16) was included for comparison. All temperatures shown on this diagram are above the critical mixing temperature of the nitric acid-nitrogen dioxide system (2). At lower temperatures three-phase behavior will be encountered for mixtures rich in nitrogen dioxide.

The influence of the weight fraction nitrogen dioxide

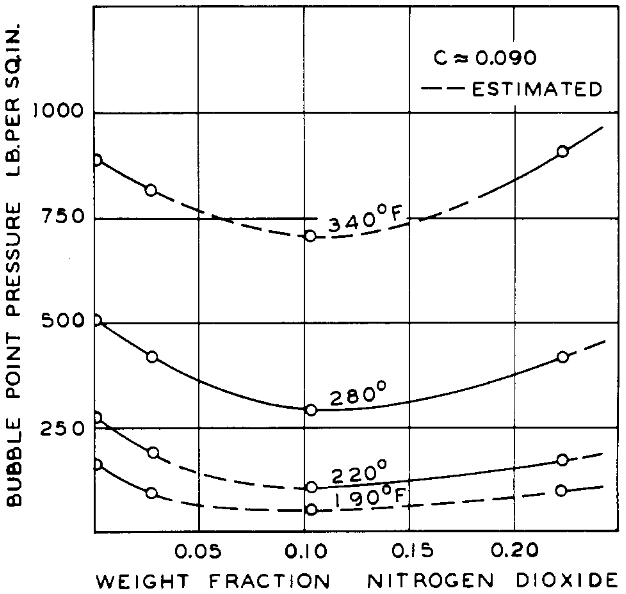

Figure 4. Effect of weight fraction nitrogen dioxide upon bubble point pressure for a value of C of 0.090

TABLE I. SPECIFIC VOLUME IN THE LIQUID PHASE OF EXPERIMENTAL MIXTURES

Pressure, Lb. /Sq. Inch	Specific Volume, Cu. Ft. /Lb. 190° F.	220° F.	280° F.	340° F.
	Mixture I			
Bubble Point	96[a] 0.01174	192[a] 0.01204	420[a] 0.01260	819[a] 0.01350
200	0.01173	0.01202		
400	0.01170	0.01197		
600	0.01169	0.01193	0.01256	
800	0.01167	0.01191	0.01251	
1000	0.01165	0.01189	0.01247	0.01344
1250	0.01163	0.01185	0.01242	0.01332
1500	0.01161	0.01183	0.01235	0.01321
1750	0.01158	0.01181	0.01231	0.01311
2000	0.01156	0.01178	0.01227	0.01304
2250	0.01153	0.01175	0.01222	0.01298
2500	0.01151	0.01173	0.01218	0.01290
2750	0.01149	0.01170	0.01216	0.01285
3000	0.01148	0.01168	0.01214	0.01279
3500	0.01145	0.01165	0.01209	0.01270
4000	0.01142	0.01162	0.01205	0.01262
4500	0.01139	0.01159	0.01201	0.01254
5000	0.01137	0.01156	0.01198	0.01250
	Mixture II			
	51[a] 0.01164	108[a] 0.01192	296[a] 0.01267	709[a] 0.01370
200	0.01162	0.01191		
400	0.01159	0.01188	0.01264	
600	0.01157	0.01185	0.01258	
800	0.01154	0.01182	0.01251	0.01364
1000	0.01152	0.01180	0.01245	0.01354
1250	0.01149	0.01175	0.01240	0.01340
1500	0.01146	0.01173	0.01234	0.01329
1750	0.01144	0.01169	0.01228	0.01318
2000	0.01142	0.01166	0.01222	0.01310
2250	0.01140	0.01162	0.01218	0.01301
2500	0.01138	0.01159	0.01214	0.01295
2750	0.01136	0.01157	0.01210	0.01289
3000	0.01134	0.01155	0.01206	0.01283
3500	0.01130	0.01151	0.01200	0.01271
4000	0.01126	0.01147	0.01195	0.01263
4500	0.01124	0.01144	0.01190	0.01256
5000	0.01122	0.01141	0.01185	0.01248
	Mixture III			
	97[a] 0.01129	171[a] 0.01160	417[a] 0.01250	904[a] 0.01361
200	0.01127	0.01159		
400	0.01125	0.01157		
600	0.01123	0.01153	0.01244	
800	0.01121	0.01150	0.01239	
1000	0.01119	0.01147	0.01233	0.01356
1250	0.01117	0.01145	0.01226	0.01343
1500	0.01115	0.01142	0.01220	0.01330
1750	0.01113	0.01139	0.01210	0.01320
2000	0.01110	0.01135	0.01208	0.01310
2250	0.01109	0.01133	0.01203	0.01301
2500	0.01105	0.01131	0.01197	0.01294
2750	0.01103	0.01128	0.01193	0.01287
3000	0.01101	0.01126	0.01187	0.01280
3500	0.01098	0.01122	0.01181	0.01267
4000	0.01096	0.01118	0.01174	0.01255
4500	0.01094	0.01113	0.01168	0.01245
5000	0.01093	0.01109	0.01163	0.01235

[a] Bubble-point pressures, lb. /sq. inch.

TABLE II. PRESSURES IN THE HETEROGENEOUS REGION FOR EXPERIMENTAL MIXTURES

Specific Volume, Cu. Ft. /Lb.	Pressure, Lb. /Sq. Inch 190° F.[a]	220° F.[a]	280° F.	340° F.
		Mixture I		
0.012	94			
0.013	90	173	403	
0.014	85	161	396	808
0.015	81	152	380	789
0.016	77	144	365	771
0.017	74	138	352	754
0.018	71	134	340	739
0.020	68	130	321	712
0.022	66	126	307	688
0.024	66	121		670
0.026	66	116		654
0.028	66	115		640
		Mixture II		
0.012		108		
0.013		108	295	
0.014		107	293	
0.015		106	291	
0.016		106	289	
0.017		105	288	
0.018		105	287	
0.020		104	284	
0.022		103	282	
0.024		102	281	
0.026		102	280	
0.028		101	278	
		Mixture III		
0.012	96	170		
0.013	96	168	415	
0.014	95	166	412	901
0.015	95	164	409	893
0.016	94	162	407	886
0.017	94	161	405	878
0.018	94	160	403	871
0.020	93	159	398	856
0.022	92	158	394	843
0.024	91	157	390	830
0.026	90	156	386	818
0.028	90	154	382	806

[a] Values at these temperatures are subject to a larger uncertainty.

upon the bubble-point pressure for several temperatures at a value of the composition parameter C of 0.090 is shown in Figure 4. The data indicate a decrease in the bubble-point pressure with increasing quantities of nitrogen dioxide followed by an increase in this pressure at weight fractions greater than 0.11.

In order to complete the portrayal of the influence of composition on the bubble-point pressure, a ternary composition diagram is presented in Figure 5. In this figure the variation of bubble-point pressure throughout the range of compositions rich in nitric acid for the ternary system nitric acid-nitrogen dioxide-water is shown for 220° F. It is emphasized that this diagram is semiquantitative in nature and subject to revision as additional experimental information is obtained. It is based upon the present investigation of the ternary system for a value of the composition parameter C of 0.090, earlier studies of nitric acid (5), nitric acid-water (3), and the nitric acid-nitrogen dioxide systems (2). In addition the behavior of a

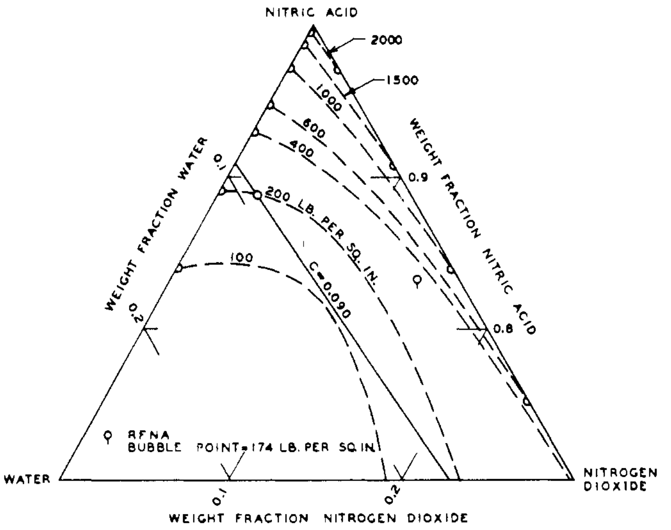

Figure 5. Influence of composition on bubble point pressure at 220° F.

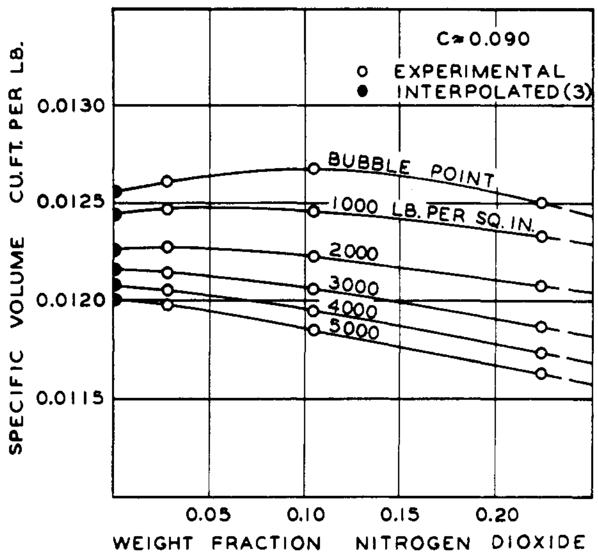

Figure 6. Effect of weight fraction nitrogen dioxide upon specific volume of the liquid at 280° F.

sample of red fuming nitric acid at physical and chemical equilibrium (12) was included for comparison. The data concerning the behavior of white fuming nitric acid (12) were open to uncertainty as a result of difficulty in establishing with accuracy the quantity of water in the sample (12) and were not included. The properties of bubble-point mixtures of the nitric acid-nitrogen dioxide-water system at a value of the composition parameter C of 0.090 are recorded in Table III. In this table the composition of each of the mixtures was included along with values of the bubble-point pressure and specific volume.

The specific volume of the restricted ternary system (14) investigated is shown in Figure 6 for 280° F. as a function of the weight fraction nitrogen dioxide under isobaric-isothermal conditions. Significant deviations from ideal solutions (9) were encountered at the lowest pressure. Such behavior is similar to that found in the study of the nitric acid-water (3) and the nitric acid-nitrogen dioxide (2) systems. There was some increase in the isothermal compressibility of the liquid phase with an increase in the weight fraction of nitrogen dioxide.

The results of this study of a restricted ternary system indicate a decrease in the bubble-point pressure at chemical and physical equilibrium with an increase in the weight fraction of nitrogen dioxide at low weight fractions of this component. Such behavior is analogous to that found for the nitric acid-nitrogen dioxide system (3). The bubble-point pressures agreed satisfactorily with those found in the earlier studies of the nitric acid-water (3) and the nitric acid-nitrogen dioxide (2) systems, as well as with that of red fuming nitric acid (12). Similar volumetric behavior was found for this system at physical equilibrium by Klemenc and Spiess (7), Wilson and Miles (21), and Taylor (19). At 100° F. the present volumetric data for physical equilibrium were in agreement with the measurements of Klemenc and Spiess (7).

TABLE III. PROPERTIES OF RESTRICTED TERNARY[a] SYSTEM AT BUBBLE POINT

Weight Fraction			190° F.		220° F.		280° F.		340° F.	
Nitrogen dioxide	Nitric acid	Water	Pressure, lb. / sq. inch	Specific volume, cu. ft. /lb.	Pressure, lb. / sq. inch	Specific volume, cu. ft. / lb.	Pressure, lb. / sq. inch	Specific volume, cu. ft. / lb.	Pressure, lb. / sq. inch	Specific volume, cu. ft./ lb.
0.0	0.909	0.091	163	0.01173[b]	272	0.01199[b]	510	0.01258	889	0.01324
0.02	0.891	0.089	111	0.01177	210	0.01201	441	0.01260	837	0.01345
0.04	0.873	0.087	77	0.01179	159	0.01202	382	0.01263	788	0.01358
0.06	0.855	0.085	59	0.01176	124	0.01200	337	0.01265	749	0.01363
0.08	0.836	0.084	52	0.01177	108	0.01198	309	0.01266	721	0.01367
0.10	0.818	0.082	50	0.01165	107	0.01194	296	0.01267	709	0.01370
0.12	0.800	0.080	53	0.01159	113	0.01189	296	0.01266	711	0.01371
0.14	0.782	0.078	60	0.01153	120	0.01184	306	0.01264	724	0.01372
0.16	0.764	0.076	69	0.01147	131	0.01178	325	0.01262	752	0.01372
0.18	0.746	0.074	78	0.01141	143	0.01172	350	0.01259	793	0.01373
0.20	0.727	0.073	87	0.01135	157	0.01167	380	0.01256	840	0.01373
0.22	0.709	0.071	97	0.01128	170	0.01162	413	0.01252	897	0.01374
0.24	0.691	0.069	107	0.01122	186	0.01156	449	0.01248	954	0.01374

[a] Limited to a value of the composition parameter of 0.090.

[b] Modified slightly from the original values (12) in the graphical smoothing operations.

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Phase Equilibria in Hydrocarbon Systems

Volumetric and Phase Behavior of the Methane–n-Heptane System

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Volumetric and phase behavior of binary hydrocarbon mixtures is of interest in predicting the behavior of fluids encountered in the production and refining of petroleum. Only limited information about the characteristics of the methane-n-heptane system is available.

Measurements of the molal volume of four mixtures of methane and n-heptane were made at pressures up to 10,000 pounds/square inch in the temperature interval between 40° and 460° F. The composition of the gas phase was determined throughout the heterogeneous region within the above-described temperature interval. The results of these measurements are presented in tabular and graphical form.

The present data are in fair agreement with earlier measurements for this system admixed with small percentages of nitrogen. The behavior was in accordance with expectations for this binary system.

In the production and refining of petroleum, use is frequently made of quantitative knowledge of the volumetric and phase behavior of hydrocarbon mixtures. Also, such information is necessary for evaluating measurements of molecular transport made under conditions which deviate from equilibrium. Mixtures of methane and n-heptane have not been intensively investigated. Boomer and Johnson (2, 3) studied this system at pressures up to approximately 3000 pounds/square inch for the temperature interval between 70° and 160° F. However, in order to approximate more closely the behavior of certain fields in Canada, these measurements were made with about 0.06 mole fraction of nitrogen present. The measurements of Boomer and Johnson were not made with the objective of establishing the partial volumetric behavior of the components and for this reason they did not furnish the data required for evaluating transient experimental measurements of diffusion coefficients. Because of the need for additional volumetric and phase equilibrium data, measurements were made of the volumetric behavior of four mixtures of methane and n-heptane at pressures up to 10,000 pounds/square inch for the temperature interval between 40° and 460° F. In addition, the composition of the gas phase in heterogeneous mixtures of the methane-n-heptane system was determined.

The volumetric behavior of each of the components has been well established. The influence of pressure and temperature upon the molal volume of methane was determined in detail (7, 8, 9) and summarized (11). These data are in good agreement with available Joule-Thomson (5) heat capacity measurements (21). The properties of n-heptane at atmospheric pressure were critically reviewed by Rossini (15). Beattie (1, 20) studied the volumetric behavior at pressures up to 4000 pounds/square inch and investigated the critical region in detail. Newitt (6) and coworkers investigated the volumetric behavior of the liquid phase at pressures up to 75,000 pounds/square inch for temperatures below 140° F. Further measurements of the volumetric behavior of n-heptane in the liquid phase, recently reported (10), were used as the basis of the volumetric behavior of n-heptane in the present study. It is believed that the volumetric and phase behavior of the two components was known with at least the accuracy for which the behavior of the four mixtures of methane and n-heptane was established.

MATERIALS

The methane employed in this study was obtained from a field in the San Joaquin Valley of California. When received at the laboratory it contained small quantities of carbon dioxide and was saturated with water. The sample was passed successively over calcium chloride, potassium hydroxide, activated charcoal, anhydrous calcium sulfate, and Ascarite at pressures in excess of 500 pounds/