properties of the bubble-point and dew-point states are recorded in Table II for even values of pressure for each of the temperatures investigated. The molal volume, composition, and the equilibrium ratios of the two components are included. The standard error of estimate of the experimental data from the smooth curves of pressure *vs.* composition was 0.003 mole fraction. This assumes that all of the uncertainty existed in composition and that none was associated with the measurement of pressure or temperature. The product of the pressure and the equilibrium ratio is shown in Figure 3. The behavior is similar to that found for other binary systems containing methane (*11, 13, 16*). The maximum two-phase pressures and temperatures and those for the critical state are presented for a series of even valued compositions in Table III. The information of Table III involves much larger uncertainties than those associated with values recorded in Table I or II because it results from extensive interpolation of the volumetric and phase equilibrium data. Uncertainties may be as large as 5% in pressure and 30° F. in temperature. The probable error in these values is much smaller but is difficult to establish with certainty.

Table III. Properties at the Unique States in the Methane-Cyclohexane System^a

Mole Fraction Methane	Pressure, P.S.I.A.	Temp., °F.	Pressure, P.S.I.A.	Temp., °F.	Pressure, P.S.I.A.	Temp., °F.
	Critical		Maxcondentherm		Maximum Pressure	
0.0	596.26^b	536^b	596.26	536	596.26	536
0.1	695	530	680	531	750	464
0.2	885	520	850	521	1,250	395
0.3	1,167	503	1,054	508	1,858	339
0.4	1,568	474	1,240	490	2,430	290
0.5	2,133	425	1,418	467	2,957	243
0.6	2,845	350	1,570	433	3,470	183
0.7	3,605	237	1,682	393	3,890	114
0.8	3,980^c	123^c	1,708	345	...	...
0.9	2,240^c	− 77^c	1,618	274	...	...
1.0	673^b	− 116^b	673	− 116	673	− 116

[a] These data are much more uncertain than directly measured quantities

[b] Based on Rossini (*14*).

[c] Estimated.

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

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Experimental information concerning the volumetric and phase behavior of the nitric acid-nitrogen dioxide-water system at physical equilibrium is available. Klemenc and Rupp (*8*) and Taylor (*22*) contributed data on the volumetric behavior of the liquid phase and on the bubble point pressures of mixtures of nitric acid and water. McKeown and Belles (*11*) reported data on the two-phase pressure of nitric acid solutions with water and nitrogen dioxide. The freezing point of the ternary system was studied by Gordon (*5*) and Küster and Kremann (*9*). Sprague (*19*) proposed an analytical expression to describe the specific weight of the liquid phase of the ternary system at physical equilibrium for atmospheric pressures.

For conditions of physicochemical equilibrium little work had been done until recently when interest was aroused by the desire to store fuming nitric acid in closed containers. The behavior of pure nitric acid (*14*) and of samples of commercial red and white fuming nitric acid (*15*) was established. In addition studies of the nitric acid-nitrogen dioxide (*2*) and the nitric acid-water (*3*) systems were made. A limited study of the volumetric and phase behavior at physicochemical equilibrium of three mixtures of nitric acid, nitrogen dioxide, and water containing approximately a fixed ratio of the weight fraction of water to the sum of the weight fractions of water and nitric acid was completed (*13*). This study at physicochemical equilibrium extended from temperatures of 190° to 340° F. and pressures up to 5000 p.s.i. Kay (*6, 7*) and Sprague (*20*) studied the pressures of this ternary system as a function of volume and temperature at physicochemical equilibrium in the heterogeneous region. Reasonable agreement exists between the several sets of data. The primary divergence seems to result from difficulties in establishing the weight fraction of water in mixtures corresponding to a composition of nearly pure nitric acid.

In spite of all the above information there appear to be insufficient data to permit prediction of the bubble point pressure as a function of temperature and composition for this ternary system at physicochemical equilibrium, or to permit the volumetric behavior of the condensed liquid and of heterogeneous mixtures of these components to be established. For this reason an additional investigation, to extend the data obtained earlier (*13*), was made. The behavior of five mixtures of nitric acid, nitrogen dioxide, and water was studied at temperatures from 190° to 340° F. and pressures up to 5000 p.s.i. The five mixtures were chosen so as to give values of the ratio of the weight fraction of water to the sum of the weight fractions of water and nitric acid of approximately 0.03 and 0.15. The value of the composition parameter for the earlier investigation (*13*) was approximately 0.090.

The term "bubble point" as used here refers to the state of a system at physicochemical equilibrium which is entirely liquid except for being in equilibrium with an infini-

Table I. Composition of Experimentally Studied Mixtures

	Mixture I	Mixture II	Mixture III	Mixture IV	Mixture V
Nitric acid	0.9273[a]	0.8101	0.7312	0.8134	0.7355
Water	0.0287	0.0261	0.0235	0.1427	0.1290
Nitrogen dioxide	0.0440	0.1638	0.2453	0.0439	0.1355
Composition parameter *C* (see Eq. 1)	0.0300	0.0312	0.0311	0.1493	0.1492

[a] All compositions expressed in weight fraction.

Table II. Specific Volume in Liquid Phase of Experimental Mixtures

Pressure, P.S.I.	190° F.	220° F.	280° F.	340° F.
		Mixture I $C \simeq 0.031$		
Bubble Point	(557)[a] 0.01014[b]	(657) 0.01040	(998) 0.01120	(1562)
200	0.01693	0.02950		
400	0.01192	0.01359	0.03775	
600	0.01012	0.01095	0.01649	
800	0.01007	0.01035	0.01289	0.03865
1000	0.01004	0.01029	0.01120	0.02143
1250	0.00999	0.01023	0.01105	0.01506
1500	0.00995	0.01017	0.01094	0.01262
1750	0.00990	0.01012	0.01084	0.01205
2000	0.00987	0.01007	0.01076	0.01185
2250	0.00983	0.01004	0.01069	0.01170
2500	0.00980	0.01000	0.01062	0.01158
2750	0.00978	0.00998	0.01056	0.01147
3000	0.00974	0.00995	0.01051	0.01137
3500	0.00971	0.00991	0.01044	0.01122
4000	0.00968	0.00987	0.01037	0.01109
4500	0.00966	0.00983	0.01030	0.01096
5000	0.00964	0.00980	0.01024	0.01084
		Mixture II $C \simeq 0.031$		
Bubble Point	(102)[a] 0.01190[b]	(182) 0.01179	(514) 0.01311	(1189) 0.01494
200	0.01116	0.01179		
400	0.01114	0.01174		
600	0.01111	0.01170	0.01362	
800	0.01108	0.01165	0.01290	
1000	0.01105	0.01159	0.01280	
1250	0.01101	0.01156	0.01270	0.01489
1500	0.01098	0.01152	0.01260	0.01467
1750	0.01096	0.01148	0.01252	0.01450
2000	0.01094	0.01142	0.01243	0.01436
2250	0.01092	0.01140	0.01238	0.01422
2500	0.01090	0.01136	0.01232	0.01408
2750	0.01088	0.01132	0.01225	0.01397
3000	0.01086	0.01129	0.01219	0.01386
3500	0.01084	0.01124	0.01210	0.01366
4000	0.01082	0.01120	0.01200	0.01348
4500	0.01079	0.01116	0.01193	0.01333
5000	0.01077	0.01111	0.01187	0.01320
		Mixture III $C \simeq 0.031$		
Bubble Point	(136)[a] 0.01177[b]	(214) 0.01239	(486) 0.01371	(1126) 0.01585
200	0.01175			
400	0.01171	0.01231		
600	0.01167	0.01221	0.01360	
800	0.01163	0.01214	0.01348	
1000	0.01159	0.01206	0.01338	
1250	0.01155	0.01198	0.01326	0.01570
1500	0.01150	0.01192	0.01315	0.01546
1750	0.01146	0.01186	0.01306	0.01526
2000	0.01141	0.01181	0.01298	0.01508
2250	0.01137	0.01175	0.01289	0.01490
2500	0.01133	0.01170	0.01281	0.01474
2750	0.01129	0.01166	0.01272	0.01462
3000	0.01127	0.01162	0.01266	0.01450
3500	0.01123	0.01156	0.01256	0.01428
4000	0.01119	0.01150	0.01248	0.01410
4500	0.01116	0.01147	0.01240	0.01394
5000	0.01113	0.01143	0.01233	0.01383

Table II. (Continued)

Pressure, P.S.I.	190° F.	220° F.	280° F.	340° F.
		Mixture IV $C \simeq 0.149$		
Bubble Point	(51)[a] 0.01188[b]	(82) 0.01222	(206) 0.01305	(446) 0.01394
200	0.01184	0.01217		
400	0.01180	0.01212	0.01295	
600	0.01177	0.01206	0.01285	0.01386
800	0.01173	0.01202	0.01276	0.01372
1000	0.01170	0.01198	0.01266	0.01360
1250	0.01167	0.01193	0.01258	0.01346
1500	0.01164	0.01188	0.01250	0.01333
1750	0.01161	0.01184	0.01243	0.01324
2000	0.01158	0.01182	0.01237	0.01314
2250	0.01156	0.01178	0.01232	0.01306
2500	0.01154	0.01176	0.01227	0.01298
2750	0.01152	0.01173	0.01223	0.01289
3000	0.01150	0.01170	0.01219	0.01282
3500	0.01149	0.01168	0.01216	0.01275
4000	0.01148	0.01166	0.01213	0.01268
4500	0.01146	0.01165	0.01210	0.01261
5000	0.01145	0.01163	0.01206	0.01256
		Mixture V $C \simeq 0.149$		
Bubble Point	(96)[a] 0.01175[b]	(152) 0.01210	(360) 0.01289	(741) 0.01376
200	0.01172	0.01208		
400	0.01168	0.01203	0.01287	
600	0.01165	0.01198	0.01278	
800	0.01162	0.01193	0.01268	0.01372
1000	0.01158	0.01188	0.01260	0.01363
1250	0.01155	0.01183	0.01252	0.01352
1500	0.01152	0.01178	0.01245	0.01341
1750	0.01150	0.01174	0.01239	0.01330
2000	0.01149	0.01171	0.01233	0.01322
2250	0.01148	0.01168	0.01228	0.01312
2500	0.01146	0.01165	0.01224	0.01305
2750	0.01144	0.01163	0.01220	0.01298
3000	0.01142	0.01160	0.01216	0.01291
3500	0.01140	0.01158	0.01212	0.01283
4000	0.01138	0.01155	0.01207	0.01275
4500	0.01136	0.01153	0.01203	0.01268
5000	0.01134	0.01151	0.01200	0.01263

[a] Values in parentheses represent bubble point pressures, p.s.i.a.
[b] Specific volume expressed in cubic feet per pound.

Table III. Deviations of Volumes for Experimentally Studied Mixtures in the Liquid Phase

	Mixture I	Mixture II	Mixture III	Av.	Mixture IV	Mixture V	Av.
		$C \simeq 0.031$			$C \simeq 0.149$		
Average deviation							
With regard to sign[a]	0.000023	0.000000	0.000020	0.000011	0.000014	0.000001	0.000008
Without regard to sign[a]	0.000031	0.000014	0.000020	0.000023	0.000030	0.000019	0.000024
Standard deviation							
Absolute[a]	0.000049	0.000022	0.000050	0.000040	0.000055	0.000022	0.000038
Relative[b]	0.46	0.19	0.41	0.35	0.46	0.18	0.32

[a] Deviation in specific volume expressed in cubic feet per pound.

[b] Relative standard deviation expressed in per cent.

tesimal amount of gas phase. It follows that the composition of the liquid phase at bubble point is identical with that of the mixture as a whole.

EQUIPMENT AND METHODS

The methods and equipment employed in this investigation were the same as those used in the study of pure nitric acid (*14*), and in the earlier part of this investigation on the volumetric and phase behavior of the nitric acid–nitrogen dioxide–water system (*13*). The sample was confined within a glass piston-cylinder combination surrounded by a fluorinated hydrocarbon confined within a stainless steel pressure vessel. Introduction and withdrawal of known quantities of the fluorinated hydrocarbon permitted known changes to be made in the total volume of the ternary system. The clearances between the piston and cylinder of the glass container were sufficiently small to reduce to insignificance diffusion of the nitric acid–nitrogen dioxide–water system to the fluorinated hydrocarbon. Past experience with this equipment has indicated probable uncertainties in the measured values of specific volume of approximately 0.6%. Calibration of the equipment as a function of pressure and temperature was required in order to take into account the compressibility of the fluorinated hydrocarbon.

The nitrogen dioxide was introduced into the piston-cylinder combination gravimetrically by utilizing weighing bomb techniques (*17*). The mixture of nitric acid and water, prepared by gravimetric methods (*13*), was introduced by a volumetric procedure which has been described (*14*). The weight of each of the components introduced into the glass piston-cylinder combination was known within 0.2%. The use of prepared mixtures of water and nitric acid of known composition permitted investigations to be made at the same ratio of nitric acid and water for a series of mixtures.

The temperature of the system was determined from that of an agitated silicone bath surrounding the stainless steel pressure vessel. The temperature of the bath was determined with a strain-free platinum resistance thermometer of the coiled filament type (*12*). This thermometer was calibrated against a similar instrument which had been submitted to the National Bureau of Standards for certification.

Table IV. Pressures in Heterogeneous Region for Experimental Mixtures

Specific Volume, Cu.Ft./Lb.	190° F.	220° F.	280° F.	340° F.
		Mixture I $C \simeq 0.031$		
0.011	473[a]	595		
0.012	393	508	896	
0.013	329	435	789	1455
0.014	278	379	715	1345
0.015	242	339	658	1255
0.016	218	312	616	1187
0.017	201	292	585	1134
0.018	188	277	559	1092
0.020	170	254	519	1032
0.025	146	218	462	937
0.030	137	198	439	876
		Mixture II $C \simeq 0.031$		
0.012	101	180		
0.013	97	177		
0.014	95	173	498	
0.015	94	170	483	1185
0.016	93	167	471	1127
0.017	91	165	462	1087
0.018	90	163	454	1057
0.020	89	159	442	1014
0.025	86	155	423	939
0.030	83	152	412	889
		Mixture III $C \simeq 0.031$		
0.012	135			
0.013	133	204		
0.014	130	193	485	
0.015	127	186	481	
0.016	124	181	477	1121
0.017	122	179	473	1094
0.018	120	178	470	1071
0.020	118	176	463	1030
0.025	113	174	450	946
0.030	109	170	438	872

Table IV. (Continued)

Specific Volume, Cu.Ft./Lb.	190° F.	220° F.	280° F.	340° F.
		Mixture IV $C \simeq 0.149$		
0.012	50			
0.013	49	81		
0.014	48	80	203	446
0.015	47	79	201	442
0.016	46	78	199	439
0.017	46	77	197	436
0.018	45	76	195	432
0.020	44	75	191	427
0.025	42	72	184	413
0.030	41	70	180	401
		Mixture V $C \simeq 0.149$		
0.012	95			
0.013	92	148	359	
0.014	90	146	352	736
0.015	88	144	345	720
0.016	86	142	340	707
0.017	84	140	335	695
0.018	82	138	331	684
0.020	81	136	323	665
0.025	78	132	309	623
0.030	75	128	298	585

[a] Pressure expressed in pounds per square inch absolute.

Table V. Deviations of Pressures for Experimentally Studied Mixtures in Heterogeneous Region

	Mixture I	Mixture II	Mixture III	Av.	Mixture IV	Mixture V	Av.
		$C \simeq 0.031$			$C = 0.149$		
Average deviation							
With regard to sign[a]	1.6	0.3	0.4	0.8	−0.6	1.1	0.2
Without regard to sign[a]	9.8	2.8	2.3	5.0	1.4	1.8	1.6
Standard deviation							
Absolute[a]	11.0	4.0	3.4	6.1	1.7	2.3	2.0
Relative[b]	2.6	1.3	1.3	1.7	1.8	1.4	1.6

[a] Deviation in pressure expressed in pounds per square inch absolute.

[b] Relative standard deviation expressed in per cent.

Temperatures of the system were believed to be known within 0.1° F. relative to the international platinum scale.

Pressures were determined by means of a piston-cylinder balance (*17*) calibrated against the vapor pressure of carbon dioxide at the ice point (*1*). Experience with the equipment indicates that the pressure within the glass piston-cylinder combination is known within 1.5 p.s.i. or 0.2%, whichever is the larger measure of uncertainty.

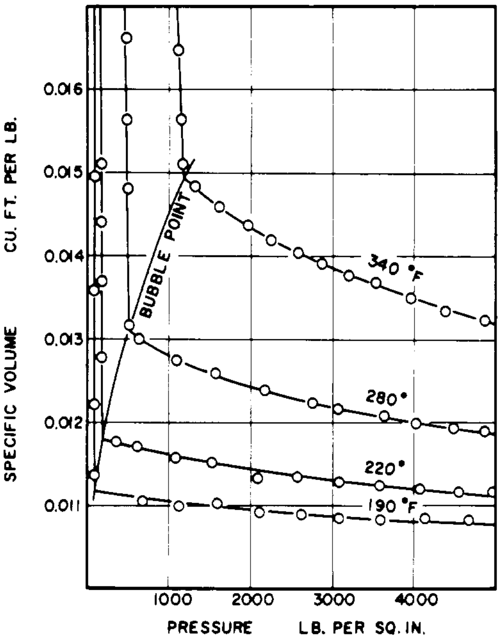

Figure 1. Experimental measurements upon mixture II

The primary uncertainty of the over-all measurements relates to the attainment of chemical equilibrium in the heterogeneous region. It is probable that errors in specific volume from nonattainment of chemical equilibrium may exceed 2% in the heterogeneous region. However, in the homogeneous liquid region it is probable that the uncertainty in measurement of specific volume does not exceed 1% over the range of pressures and temperatures recorded here. The above measures of uncertainty assume negligible errors in pressure and temperature.

Physical equilibrium was obtained by oscillating the steel pressure vessel. A small glass ball, which rolled from one end of the interior of the glass piston-cylinder combination to the other, aided in the attainment of physical equilibrium.

MATERIALS

As in previous investigations (*13*), the nitric acid was prepared from potassium nitrate and sulfuric acid by established methods (*4*). It was redistilled at a pressure below 0.005 inch of mercury and the central portion of the overhead was retained for use. A specific weight of 93.825 pounds per cubic foot at 77° F. was found for the acid employed. Its value may be compared with 93.873 pounds per cubic foot reported by Stern and Kay (*21*) and 93.755 pounds per cubic foot by Klemenc and Rupp (*8*). The specific conductance of nitric acid similarly prepared in the same equipment was 3.77 reciprocal ohm-cm. at 32° F. (*16*). This information indicates that the nitric acid employed contained less than 0.002 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 purchased from commercial sources was

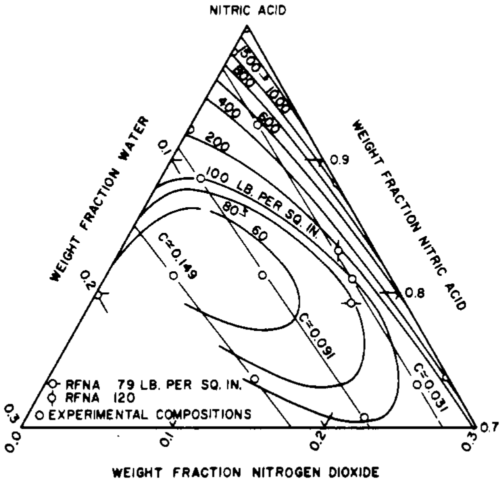

Figure 2. Bubble point pressures at 190° F.

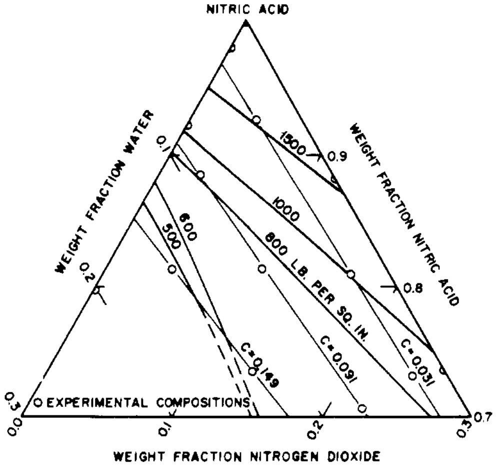

Figure 3. Bubble point pressures at 340° F.

subjected to two sequential fractionations at nearly atmospheric pressure in a column provided with 16 glass plates. The central third of the overhead was collected from each of the two distillations which were carried out at reflux ratios of approximately 25. The nitrogen dioxide was dried over phosphorus pentoxide and stored in stainless steel weighing bombs (*17*). In order to simplify the discussion, the term nitrogen dioxide as employed in this paper refers to the equilibrium mixtures of nitrogen dioxide and nitrogen tetroxide. All results are presented upon a weight basis so no ambiguity results from this simplification in terminology.

APPROACH TO EQUILIBRIUM

Only a short period was required to attain physical equilibrium under the conditions of agitation used. However, in order to obtain chemical equilibrium, widely differing periods of time were required. An increase in temperature or in weight fraction of nitrogen dioxide materially decreased the time required. This behavior accords with the trends found in the nitric acid-water (*3*) and in the nitric acid-nitrogen dioxide (*2*) systems. These trends have already been reported (*2, 3*). However, primary uncertainty in regard to the volumetric behavior in the heterogeneous region results from difficulties in obtaining chemical equilibrium in heterogeneous mixtures of nitric acid containing significant quantities of water at a temperature of 190° F.

BEHAVIOR AT PHYSICOCHEMICAL EQUILIBRIUM

Compositions of the five mixtures investigated in this study are set forth in Table I. The compositions, *n*, are

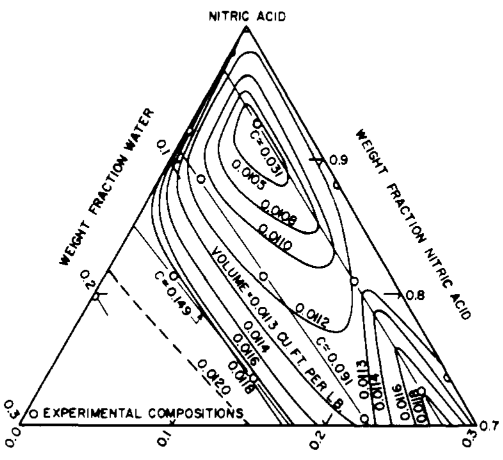

Figure 4. Estimated specific volumes at bubble point for 190° F.

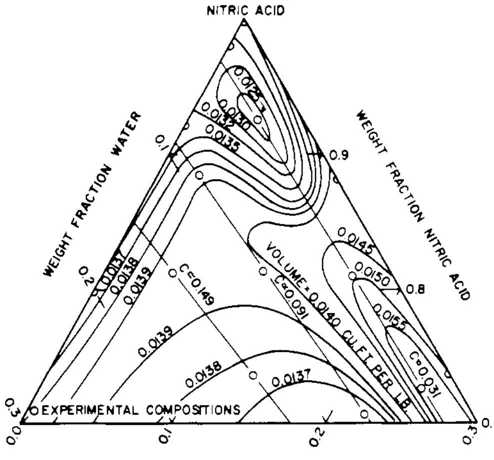

Figure 5. Estimated specific volumes at bubble point for 340° F.

Table VI. Properties of System at Bubble Point

Weight Fraction										
Nitrogen dioxide	Nitric acid	Water	Pressure, P.S.I.	Specific Volume, Cu.Ft./Lb.	Pressure, P.S.I.	Specific Volume, Cu.Ft./Lb.	Pressure, P.S.I.	Specific Volume, Cu.Ft./Lb.	Pressure, P.S.I.	Specific Volume, Cu.Ft./Lb.
			190°F.		220°F.		280°F.		340°F.	
					$C \simeq 0.031$					
0.00	0.969	0.031	776	0.01143	931	0.01172	1329	0.01237	1806	0.01316
0.02	0.950	0.030	687	0.01075^a	818	0.01099^a	1188	0.01170^a	1704	0.01263^a
0.04	0.930	0.030	574	0.01017^a	687	0.01043^a	1034	0.01123^a	1591	0.01223^a
0.06	0.911	0.029	468	0.01027	569	0.01051	896	0.01142	1489	0.01249
0.08	0.892	0.028	373	0.01045	467	0.01078	778	0.01179	1403	0.01305
0.10	0.872	0.028	290	0.01064	373	0.01105	679	0.01216	1338	0.01360
0.12	0.853	0.027	211	0.01082	286	0.01130	598	0.01249	1280	0.01409
0.14	0.833	0.027	147	0.01099	223	0.01153	541	0.01279	1231	0.01452
0.16	0.814	0.026	107	0.01116	187	0.01174	514	0.01306	1193	0.01489
0.18	0.795	0.025	91	0.01132	173	0.01194	502	0.01327	1167	0.01519
0.20	0.775	0.025	92	0.01148	176	0.01210	495	0.01345	1149	0.01544
0.22	0.756	0.024	108	0.01162	189	0.01225	490	0.01359	1137	0.01565
0.24	0.736	0.024	129	0.01175	208	0.01237	488	0.01369	1128	0.01580
					$C \simeq 0.149$					
0.00	0.851	0.149	96	0.01189	114	0.01217	235	0.01276	437	0.01339
0.02	0.834	0.146	59	0.01189^a	94	0.01222^a	215	0.01296^a	437	0.01382^a
0.04	0.817	0.143	52	0.01188^a	88	0.01222^a	205	0.01304^a	444	0.01393^a
0.06	0.800	0.140	54	0.01186	85	0.01221	211	0.01306	466	0.01394
0.08	0.783	0.137	63	0.01184	96	0.01218	236	0.01303	524	0.01391
0.10	0.766	0.134	73	0.01182	113	0.01216	274	0.01299	599	0.01387
0.12	0.749	0.131	84	0.01178	134	0.01213	320	0.01293	676	0.01381
0.14	0.732	0.128	98^b	0.01174^b	157^b	0.01209^b	372^b	0.01287^b	760^b	0.01375^b
0.16	0.715	0.125	112^b	0.01171^b	181^b	0.01205^b	428^b	0.01281^b	845^b	0.01368^b

[a] Interpolated.
[b] Extrapolated.

Table VII. Specific Volume of the Liquid Phase for Even Values of Weight Fraction of Nitrogen Dioxide

$C \simeq 0.031$
0.05 Weight Fraction Nitrogen Dioxide

Pressure, P.S.I.	190° F.	220° F.	280° F.	340° F.
	(518)[a]	(621)	(959)	(1540)
Bubble Point	0.01017[b]	0.01041	0.01125	0.01226
200				
400				
600	0.01015			
800	0.01010	0.01036		
1000	0.01007	0.01031	0.01123	
1250	0.01003	0.01025	0.01110	
1500	0.00999	0.01020	0.01098	
1750	0.00995	0.01015	0.01089	0.01207
2000	0.00992	0.01012	0.01081	0.01192
2250	0.00990	0.01008	0.01074	0.01179
2500	0.00987	0.01005	0.01067	0.01168
2750	0.00984	0.01002	0.01062	0.01157
3000	0.00982	0.01000	0.01056	0.01149
3500	0.00979	0.00995	0.01048	0.01133
4000	0.00975	0.00991	0.01040	0.01120
4500	0.00972	0.00987	0.01034	0.01108
5000	0.00969	0.00984	0.01028	0.01097

$C \simeq 0.031$
0.10 Weight Fraction Nitrogen Dioxide

Pressure, P.S.I.	190° F.	220° F.	280° F.	340° F.
	(290)[a]	(373)	(679)	(1338)
Bubble Point	0.01064[b]	0.01105	0.01216	0.01360
200				
400	0.01063	0.01104		
600	0.01060	0.01101		
800	0.01056	0.01097	0.01209	
1000	0.01053	0.01095	0.01198	
1250	0.01049	0.01090	0.01187	
1500	0.01046	0.01087	0.01177	0.01346
1750	0.01043	0.01083	0.01169	0.01329
2000	0.01040	0.01079	0.01163	0.01316
2250	0.01038	0.01076	0.01156	0.01305
2500	0.01036	0.01072	0.01150	0.01294
2750	0.01034	0.01070	0.01144	0.01284
3000	0.01032	0.01067	0.01140	0.01275
3500	0.01029	0.01062	0.01131	0.01258
4000	0.01027	0.01058	0.01124	0.01243
4500	0.01024	0.01054	0.01117	0.01228
5000	0.01023	0.01051	0.01111	0.01215

$C \simeq 0.031$
0.15 Weight Fraction Nitrogen Dioxide

Pressure, P.S.I.	190° F.	220° F.	280° F.	340° F.
	(124)[a]	(201)	(523)	(1211)
Bubble Point	0.01108[b]	0.01164	0.01296	0.01472
200	0.01106			
400	0.01103	0.01159		
600	0.01100	0.01154	0.01289	
800	0.01097	0.01150	0.01276	
1000	0.01095	0.01147	0.01265	
1250	0.01091	0.01142	0.01253	0.01466
1500	0.01088	0.01137	0.01243	0.01446
1750	0.01085	0.01134	0.01233	0.01430
2000	0.01083	0.01130	0.01227	0.01416
2250	0.01080	0.01127	0.01220	0.01401
2500	0.01078	0.01123	0.01214	0.01389
2750	0.01077	0.01120	0.01208	0.01377
3000	0.01076	0.01118	0.01204	0.01367
3500	0.01073	0.01113	0.01195	0.01349
4000	0.01071	0.01109	0.01187	0.01332
4500	0.01069	0.01105	0.01180	0.01316
5000	0.01067	0.01100	0.01173	0.01302

$C \simeq 0.031$
0.20 Weight Fraction Nitrogen Dioxide

Pressure, P.S.I.	190° F.	220° F.	280° F.	340° F.
	(92)[a]	(176)	(495)	(1149)
Bubble Point	0.01148[b]	0.01210	0.01345	0.01544
200	0.01145	0.01209		
400	0.01140	0.01201		
600	0.01137	0.01195	0.01335	
800	0.01133	0.01189	0.01321	
1000	0.01130	0.01184	0.01311	
1250	0.01127	0.01178	0.01299	0.01532
1500	0.01124	0.01173	0.01289	0.01509
1750	0.01120	0.01169	0.01280	0.01490
2000	0.01118	0.01165	0.01273	0.01475
2250	0.01116	0.01161	0.01266	0.01460
2500	0.01114	0.01157	0.01259	0.01446
2750	0.01112	0.01154	0.01253	0.01434
3000	0.01110	0.01151	0.01248	0.01423
3500	0.01105	0.01145	0.01238	0.01404
4000	0.01104	0.01140	0.01229	0.01386
4500	0.01101	0.01135	0.01221	0.01370
5000	0.01098	0.01131	0.01214	0.01355

$C \simeq 0.149$
0.05 Weight Fraction Nitrogen Dioxide

Pressure, P.S.I.	190° F.	220° F.	280° F.	340° F.
	(52)[a]	(81)	(205)	(450)
Bubble Point	0.01187[b]	0.01222	0.01306	0.01394
200	0.01183	0.01218		
400	0.01178	0.01211	0.01294	
600	0.01174	0.01206	0.01283	0.01385
800	0.01171	0.01201	0.01273	0.01372
1000	0.01168	0.01196	0.01265	0.01362
1250	0.01165	0.01191	0.01257	0.01347
1500	0.01162	0.01187	0.01249	0.01335
1750	0.01160	0.01182	0.01243	0.01324
2000	0.01157	0.01179	0.01237	0.01313
2250	0.01156	0.01178	0.01232	0.01305
2500	0.01154	0.01173	0.01228	0.01296
2750	0.01152	0.01171	0.01224	0.01290
3000	0.01151	0.01169	0.01221	0.01284
3500	0.01148	0.01166	0.01216	0.01275
4000	0.01146	0.01164	0.01211	0.01268
4500	0.01145	0.01163	0.01208	0.01262
5000	0.01144	0.01162	0.01206	0.01256

$C \simeq 0.149$
0.10 Weight Fraction Nitrogen Dioxide

Pressure, P.S.I.	190° F.	220° F.	280° F.	340° F.
	(73)[a]	(113)	(274)	(599)
Bubble Point	0.01182[b]	0.01216	0.01299	0.01387
200	0.01178	0.01213		
400	0.01173	0.01205	0.01293	
600	0.01169	0.01201	0.01281	0.01387
800	0.01166	0.01195	0.01271	0.01375
1000	0.01162	0.01190	0.01264	0.01364
1250	0.01159	0.01185	0.01254	0.01350
1500	0.01156	0.01180	0.01246	0.01338
1750	0.01154	0.01176	0.01240	0.01326
2000	0.01152	0.01173	0.01234	0.01317
2250	0.01150	0.01170	0.01229	0.01308
2500	0.01148	0.01167	0.01225	0.01300
2750	0.01146	0.01164	0.01221	0.01293
3000	0.01144	0.01162	0.01217	0.01288
3500	0.01142	0.01159	0.01211	0.01278
4000	0.01140	0.01156	0.01206	0.01270
4500	0.01139	0.01154	0.01202	0.01264
5000	0.01137	0.01153	0.01199	0.01260

Table VII. (Continued)

Pressure, P.S.I.	190° F.	220° F.	280° F.	340° F.
	$C \simeq 0.149$ 0.15 Weight Fraction Nitrogen Dioxide			
	(104)[a]	(169)	(399)	(802)
Bubble Point	0.01173[b]	0.01208	0.01284	0.01371
200	0.01171	0.01206		
400	0.01167	0.01200	0.01284	
600	0.01164	0.01195	0.01274	
800	0.01161	0.01190	0.01265	
1000	0.01159	0.01185	0.01258	0.01362
1250	0.01156	0.01180	0.01250	0.01350
1500	0.01153	0.01176	0.01243	0.01339
1750	0.01150	0.01172	0.01237	0.01329
2000	0.01148	0.01169	0.01232	0.01320
2250	0.01146	0.01166	0.01228	0.01312
2500	0.01144	0.01163	0.01224	0.01304
2750	0.01143	0.01161	0.01220	0.01297
3000	0.01142	0.01160	0.01217	0.01292
3500	0.01139	0.01156	0.01211	0.01282
4000	0.01137	0.01154	0.01207	0.01275
4500	0.01135	0.01152	0.01203	0.01268
5000	0.01134	0.01150	0.01200	0.01264

[a] Values in parentheses represent bubble point pressures expressed in pounds per square inch absolute.

[b] Specific volume expressed in cubic feet per pound.

expressed in weight fraction, and values of a composition parameter are included. This parameter is defined as follows:

$$C = \frac{n_{H_2O}}{n_{H_2O} + n_{HNO_3}} \qquad (1)$$

The mixtures were restricted to two values of the composition parameter, 0.03 and 0.15.

The specific volume was determined as a function of pressure for three or four temperatures in the interval between 190° and 340° F. Pressures were carried to a maximum of 5000 p.s.i. The experimental data for each mixture investigated are recorded for the liquid phase in Table II. These data have been smoothed only with respect to pressure and temperature. The average and standard deviations of the primary experimental values from the data of Table II are recorded in Table III.

Table IV records pressures for even values of specific volume in the heterogeneous region for each of the five mixtures investigated. The corresponding average and standard deviations are shown in Table V for each of the five experimental mixtures. As a matter of interest a typical set of experimental results for one of the mixtures is shown in Figure 1. The curves shown correspond to those obtained from smoothing the data with respect to temperature, pressure, and composition.

By carrying out the investigations at constant values of the composition parameter C it was possible to accomplish the initial smoothing with respect to composition by treating the two groups of mixtures as restricted ternary systems (*18*). The phase equilibrium and volumetric data for each of the two restricted ternary systems recorded in Table II were smoothed with respect to composition with other data. These included measurements obtained for a value of the composition parameter of approximately 0.090 (*13*), as well as for measurements upon the nitric acid (*14*), nitric acid-water (*3*), and the nitric acid-nitrogen dioxide (*2*) systems. The behavior of the two restricted ternary systems presented here is similar to that reported earlier for a system with a value of composition parameter of 0.090 (*13*). For this reason it does not appear necessary to consider in detail the behavior of these two sets of mixtures when treated as restricted ternary systems.

The bubble point pressure at 190° F. for a portion of the nitric acid-nitrogen dioxide-water system at physicochemical equilibrium is shown as a parameter in Figure 2, similar information for a temperature of 340° F. is depicted in Figure 3. In establishing this behavior, available information concerning the nitric acid-water (*3*) and the nitric acid-nitrogen dioxide system (*2*), as well as concerning the behavior of pure nitric acid (*14*), was used. The compositions at which experimental data were available are included upon these diagrams in order to illustrate the distribution of experimental information. Furthermore, data obtained upon the behavior of a sample of red fuming nitric acid at physicochemical equilibrium (*15*) are included for comparison in Figure 2. Similar information for a white fuming nitric acid (*15*) is not included on account of uncertainty as to the quantity of water in the sample.

The specific volume at bubble point is shown as a parameter in Figures 4 and 5 for temperatures of 190° and 340° F. Again the compositions for which experimental data were available are indicated on the diagrams. Marked deviations from ideal solutions are encountered, particu-

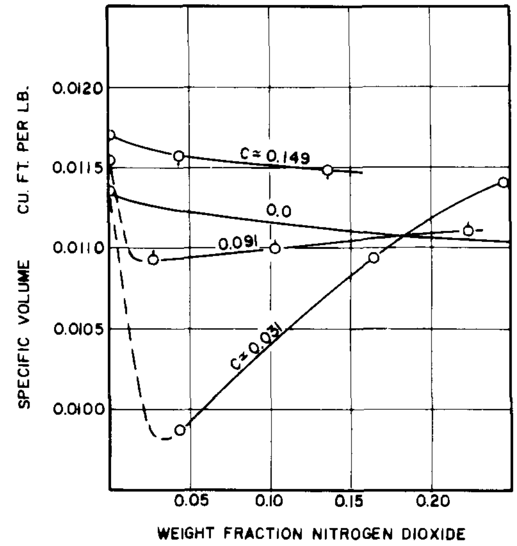

Figure 6. Specific volumes at 2000 pounds per square inch for 190° F.

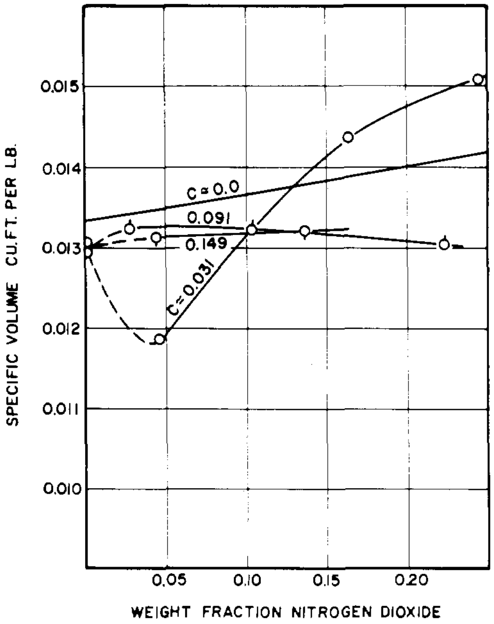

Figure 7. Specific volumes at 2000 pounds per square inch for 340° F.

larly at compositions near pure nitric acid. In fact, the graphical portrayal of the results of the earlier investigation (*13*) did not take into account some of the more marked variations from ideal behavior which were later confirmed by further measurements, reported here. For this reason, some of the data presented in Figures 4 and 5 do not agree in detail at compositions near the nitric acid-water system with those published earlier (*13*).

Table VI records the pressure and the specific volume at bubble point of a number of ternary mixtures corresponding to values of the composition parameter of 0.031 and 0.149. The specific volume in the condensed liquid region as a function of pressure is recorded for seven different compositions in Table VII. These compositions correspond to values of the composition parameter of 0.031 and 0.149.

The marked digressions from ideal solutions at a pressure of 2000 p.s.i. are shown in Figures 6 and 7, where the specific volumes for three different restricted ternary systems and one binary system are depicted at temperatures of 190° and 340° F. The data indicate a marked decrease in the specific volume with increase in weight fraction nitrogen dioxide, followed by a gradual increase in specific volume with further increase in weight fraction nitrogen dioxide for two restricted ternary systems at 190° F. These trends continue in the case of only one restricted ternary system corresponding to a value of parameter C of 0.031 at a temperature of 340° F. The deviation from ideal solutions is several times that of the experimental uncertainty. This type of behavior was found in the initial investigation (*13*), although not sufficient credence was placed in the experimental data to interpret the divergences from ideal solutions (*10*) as being as large as they are shown here. Further experimental work would be desirable to confirm this surprisingly complicated behavior.

There is shown in Figure 8 in projection the bubble point pressure of the nitric acid-nitrogen dioxide-water system at 190° F. The marked increase in the bubble point pressures as compositions approaching that of pure nitric acid are reached is clearly evident. The great difference of bubble point pressures realized at physical equilibrium (*22*) from those found for physicochemical equilibrium and as reported here is evidence of the significant rearrangements which occur during the attainment of chemical equilibrium in this ternary system.

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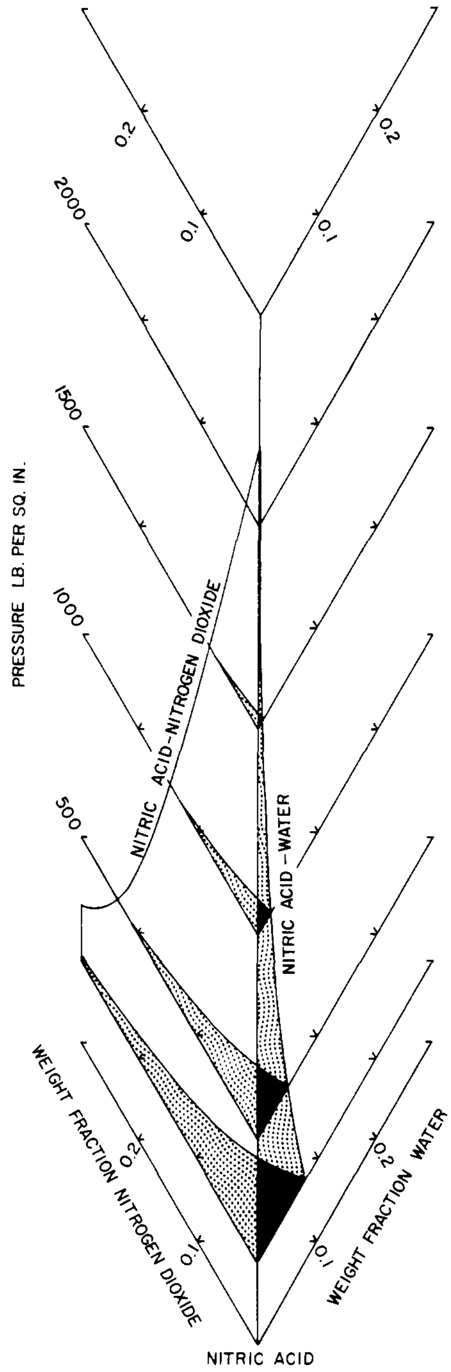

Figure 8. Influence of composition on bubble point pressure for 190° F.

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