

Figure 14. ASTM D-86 distillation and flash equilibrium data at atmospheric pressure for sample A

curve is flatter. Figure 14, showing a plot of both the ASTM D-86 distillation curve and the flash equilibrium curve at atmospheric pressure for sample A, illustrates this point. This is in accord with the expected results for these types of data (3, 4, 7). On the flash curve, the point corresponding to the ASTM initial boiling point is high because of the suppressing effect of the heavy ends. The reduced slope and lower end point are caused by the partial pressure effect of the light ends.

The effect of pressure is, of course, to reduce vaporiza-

tion at a given temperature; however this becomes less pronounced at elevated pressures. For example, in the case of sample A an increase in the pressure from 1 to 3 atm. has approximately the same effect on vaporization as an increase from 10 to 20 atm. Thus, at 390° F. (see Figure 5), increasing the pressure from 1 to 3 atm. decreases the volume per cent overhead from 100 to 28; while at 595° F. increasing the pressure from 10 to 20 atm. results in an almost identical decrease in overhead of 99 to 24.

ACKNOWLEDGMENT

The author wishes to express his appreciation to H. E. Luntz and J. W. Conwell for their many helpful suggestions concerning the obtaining, calculation, and presentation of the data included in this paper and to Continental Oil Co. for permission to publish this work.

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Received for review July 2, 1956. Accepted October 26, 1956.

Phase Relations of Nitric Acid-Nitrogen Dioxide and Nitric Acid-Water Mixtures at Physicochemical Equilibrium

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The volumetric phase relations of liquid nitric acid at physical and chemical equilibrium have been presented (5). It was shown that the pure acid is unstable at temperatures above its melting point ($-41.59^{\circ}\text{C}.$) and that it develops a high gas pressure when stored in a closed container if the ratio of the vapor space to the total volume of the container is small. As the concentrated nitric acid of commerce contains excess water and nitrogen dioxide, it is of interest in connection with the storage and handling of the acid to know the effect of these additives on its equilibrium pressure.

To obtain the required data, an investigation of the volumetric phase relations of the system nitric acid-nitrogen

dioxide-water is necessary. As a preliminary step to such an investigation, the phase relations of nitric acid-nitrogen dioxide mixtures containing up to 15% by weight of nitrogen dioxide and of nitric acid-water mixtures containing up to 5% by weight of water were determined under conditions of physicochemical equilibrium. The selected concentration range is of particular interest in the field of liquid rocket propellants. The measurements were made between 85° and $150^{\circ}\text{C}.$ and for the ratios of the vapor volume to total volume, (V^g/V), between 0.8 and near the bubble point. The results are summarized here.

Corcoran, Reamer, Duffy, and Sage (1, 2) have investigated the volumetric and phase behavior of the nitric acid-nitrogen dioxide and the nitric acid-water systems, but their

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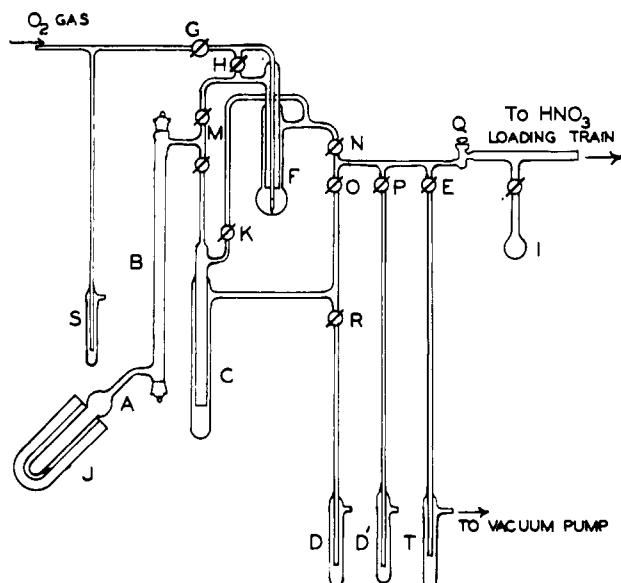


Figure 1. Apparatus for preparation of nitrogen dioxide

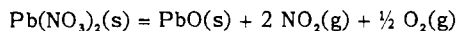
measurements are confined principally to a region of lower specific volume than was covered in the present investigation.

PREPARATION OF MATERIALS

Nitric acid was prepared by reaction of 100% sulfuric acid with anhydrous potassium nitrate at 0°C. in the complete absence of air; the acid was collected as a solid at liquid nitrogen temperature (5). The acid showed by chemical analysis a total acidity of $99.98 \pm 0.05\%$ nitric acid, with no trace of nitrogen dioxide or sulfur trioxide.

Pure water was obtained by the double distillation of an acidified aqueous solution of potassium permanganate.

Nitrogen dioxide was prepared by the thermal decomposition of pure, dry, lead nitrate according to the equation:



The term nitrogen dioxide is used in this investigation to describe an equilibrium mixture of NO_2 and N_2O_4 .

The apparatus for the generation and purification of the product is shown in Figure 1 and was constructed of borosilicate glass. The lead nitrate was decomposed in the reactor, A, which was enclosed and heated by the electric furnace, J. The gaseous nitrogen dioxide-oxygen mixture was passed through the drying tube, B, filled with phosphorus pentoxide suspended on loosely packed glass wool, to the trap, C, where the nitrogen dioxide was frozen out by surrounding C with a bath of dry ice and acetone. The re-

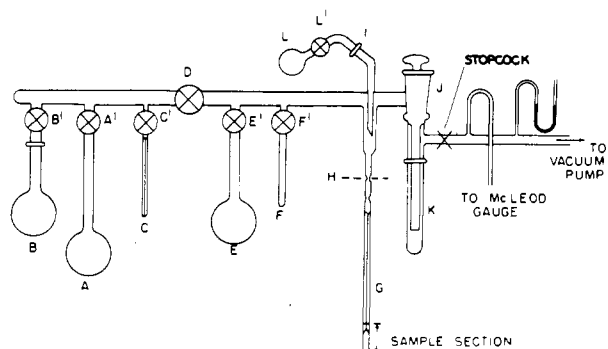


Figure 2. Apparatus for preparation of nitric acid-water and nitric acid-nitrogen dioxide mixtures

maining oxygen gas built up pressure and escaped to the atmosphere through the barometric mercury bubbler, D.

When a sufficient amount of nitrogen dioxide had been collected in C, the reactor was cooled, the system was evacuated through stopcocks O and E, and the cocks were closed. The cooling bath was removed from around C and placed around trap F and, by proper manipulation of the stopcocks, the nitrogen dioxide was transferred to F and frozen. During this operation stopcocks R and P to the mercury bubblers, D and D', were closed to prevent the nitrogen dioxide gas from coming in contact with the mercury in the wells of the bubblers.

The nitrogen dioxide in trap F was allowed to melt and pure oxygen gas was bubbled through the liquid by opening stopcock G and adjusting cock H. By bringing the liquid in contact with oxygen gas, traces of the lower oxides of nitrogen were oxidized to nitrogen dioxide.

After passage through the liquid nitrogen dioxide, the oxygen gas with traces of nitrogen dioxide was directed through stopcock K to cold trap C, where the nitrogen dioxide was frozen out while the oxygen escaped as before, through trap D.

The liquid nitrogen dioxide was brought in contact with the oxygen gas for 1 hour, after which it was frozen and the system was evacuated through cock E. The purified nitrogen dioxide was transferred by sublimation to the storage flask, I, which was part of the apparatus for preparing the mixtures to be studied. The product, a crystalline white solid, was kept in the solid state by surrounding the storage flask with a dry ice-acetone bath.

PREPARATION OF MIXTURES

The apparatus for the preparation of nitric acid-nitrogen dioxide and nitric acid-water mixtures and for their loading into the experimental tube in the complete absence of air, is shown in Figure 2. The apparatus was constructed of borosilicate glass and was evacuated by means of a mercury diffusion pump backed by a mechanical pump. All ground joints were lubricated with an inert perfluoro grease in order to eliminate any possible contamination of the acid by the lubricant. The pure nitric acid was stored in bulb E, while the second component, either water or nitrogen dioxide, was charged to bulb B. The latter substances were deaerated by repeated distillation between bulbs A and B. The distillate was frozen after each operation and the residual noncondensable gas over the solid was pumped off. Tubes F and C, as well as the sample section of the experimental tube, G, were calibrated with mercury and a table was prepared for each tube, expressing the total volume to any level of the tube in terms of the length from the sealed end which served as a reference. This distance was measured by means of a cathetometer reading to 0.05 mm. Tube G, in which the volumetric properties of the sample were measured, was sealed directly to the high vacuum line.

A sample was prepared in the following manner. The volumes of the separate components necessary to make a mixture of a given specific volume and composition were com-

Table I. Time Required to Reach 90% of Equilibrium Pressure at 85°C. as a Function of V^G/V and Initial Composition

Initial Composition, Wt. %			Time, Min., V^G/V				
HNO ₃	NO ₂	H ₂ O	0.1	0.2	0.4	0.6	0.8
85.0	15.0	0.0	95	110	145	190	260
92.5	7.5	0.0	145	165	215	280	365
100.0	0.0	0.0	190	210	270	340	430
97.5	0.0	2.5	470	540	710	930	1220
95.0	0.0	5.0	800	900	1150	1460	1850

Table II. Experimental Equilibrium Decomposition Pressures of Mixtures of Nitric Acid and Nitrogen Dioxide

Specific Vol., Cu. Foot/Pound											
0.04416			0.01861			0.01381			0.01244		
NO ₂ , Weight Per Cent											
7.49			7.49			7.52			7.52		
Temp., °C.	Equil. pressure, lb./sq. inch abs.	V ^G /V	Equil. pressure, lb./sq. inch abs.	V ^G /V	Equil. pressure, lb./sq. inch abs.	V ^G /V	Equil. pressure, lb./sq. inch abs.	V ^G /V	Equil. pressure, lb./sq. inch abs.	V ^G /V	
85.0	152	0.765	359	0.421	632	0.211	878	0.113			
95.0	189	0.763	413	0.413	714	0.199	987	0.100			
105.0	234	0.762	481	0.405	810	0.186	1115	0.084			
115.0	295	0.761	564	0.396	927	0.171					
125.0	366	0.760	658	0.386	1051	0.156					
135.0	456	0.760	780	0.376	1200	0.138					
150.0	626	0.759	1012	0.360							

Specific Vol., Cu. Foot/Pound											
0.04562			0.01848			0.01340			0.01208		
NO ₂ , Weight Per Cent											
15.01			15.00			15.03			15.00		
Temp., °C.	Equil. pressure, lb./sq. inch abs.	V ^G /V	Equil. pressure, lb./sq. inch abs.	V ^G /V	Equil. pressure, lb./sq. inch abs.	V ^G /V	Equil. pressure, lb./sq. inch abs.	V ^G /V	Equil. pressure, lb./sq. inch abs.	V ^G /V	
85.0	133	0.772	270	0.421	479	0.191	640	0.100			
95.0	170	0.771	326	0.413	562	0.178	747	0.085			
105.0	220	0.770	396	0.404	661	0.164	876	0.068			
115.0	286	0.770	484	0.393	782	0.147	1030	0.050			
125.0	366	0.769	583	0.384	916	0.131	1197	0.029			
135.0	464	0.769	711	0.372	1085	0.108	1406	0.005			
150.0	646	0.768	985	0.355	1401	0.070					

puted for a reference temperature of 0°C. from a knowledge of the individual densities, and expressed in terms of the length from the sealed end of the volumetric tubes, *F* (for nitric acid) and *C* (for nitrogen dioxide or water). Corrections were applied for the volume of the complement of the liquid meniscus and for the liquid volume equivalent of the vapor phase in equilibrium with the liquid. The following

orthobaric densities of the components at 0°C. were used: nitrogen dioxide, $\rho_L = 1.4905$ grams per cc. (4); $\rho_V = 0.00135$ grams per cc. [calculated from the vapor pressure (3) and degree of dissociation of nitrogen tetroxide (7) assuming the vapor to be a perfect gas]; nitric acid, $\rho_L = 1.5492$ grams per cc. (6); water, $\rho_L = 0.9999$.

The position of the liquid meniscus in the volumetric

Table III. Experimental Equilibrium Decomposition Pressures of Mixtures of Nitric Acid and Water

Specific Vol., Cu. Foot/Pound											
0.03689			0.01759			0.01426			0.01277		
H ₂ O, Weight Per Cent											
2.50			2.50			2.50			2.50		
Temp., °C.	Equil. pressure, lb./sq. inch abs.	V ^G /V	Equil. pressure, lb./sq. inch abs.	V ^G /V	Equil. pressure, lb./sq. inch abs.	V ^G /V	Equil. pressure, lb./sq. inch abs.	V ^G /V	Equil. pressure, lb./sq. inch abs.	V ^G /V	
85.0	138	0.708	328	0.374	516	0.216	739	0.116			
95.0	163	0.706	373	0.365	572	0.206	820	0.103			
105.0	199	0.705	430	0.357	654	0.193	925	0.089			
115.0	246	0.704	498	0.349	745	0.181	1044	0.075			
125.0	302	0.702	576	0.340	844	0.169	1176	0.060			
135.0	375	0.701	678	0.329	964	0.155	1342	0.042			
150.0	516	0.700	861	0.313	1202	0.131	1649	0.005			

Specific Vol., Cu. Foot/Pound													
0.05633			0.01961			0.01406			0.01252			0.01190	
H ₂ O, Weight Per Cent													
4.99			4.81			5.02			5.02			5.00	
Temp., °C.	Equil. pressure, lb./sq. inch abs.	V ^G /V	Equil. pressure, lb./sq. inch abs.	V ^G /V	Equil. pressure, lb./sq. inch abs.	V ^G /V	Equil. pressure, lb./sq. inch abs.	V ^G /V	Equil. pressure, lb./sq. inch abs.	V ^G /V	Equil. pressure, lb./sq. inch abs.	V ^G /V	
85.0	76	0.814	202	0.429	348	0.188	493	0.086	595	0.048			
95.0	97	0.813	231	0.421	395	0.178	561	0.074	679	0.037			
105.0	126	0.811	275	0.413	458	0.166	632	0.060	782	0.020			
115.0	161	0.809	329	0.406	535	0.154	747	0.045	897	0.005			
125.0	206	0.808	390	0.398	620	0.142	857	0.032	983 ^a	0.000			
135.0	263	0.807	471	0.390	730	0.128	993	0.016					
150.0	372	0.805	630	0.378	942	0.104	1207 ^a	0.000					

^aBubble point pressure.

Table IV. Phase Relations in Nitric Acid-Nitrogen Dioxide System at Physicochemical Equilibrium

V^G/V	Temp., °C.	0.00 Weight % NO ₂		4.00 Weight % NO ₂		8.00 Weight % NO ₂		12.00 Weight % NO ₂		16.00 Weight % NO ₂	
		Specific volume, cu.ft./ lb.	Equilibrium pressure, lb./sq. inch abs.	Specific volume, cu.ft./ lb.	Equilibrium pressure, lb./sq. inch abs.	Specific volume, cu.ft./ lb.	Equilibrium pressure, lb./sq. inch abs.	Specific volume, cu.ft./ lb.	Equilibrium pressure, lb./sq. inch abs.	Specific volume, cu.ft./ lb.	Equilibrium pressure, lb./sq. inch abs.
0.1	85	0.01232	1390	0.01228	1093	0.01224	905	0.01220	750	0.01216	604
0.2	85	0.01375	934	0.01370	765	0.01365	645	0.01360	539	0.01355	443
0.3	85	0.01563	680	0.01556	571	0.01549	485	0.01542	407	0.01535	338
0.4	85	0.01809	512	0.01798	432	0.01787	370	0.01776	316	0.01765	270
0.5	85	0.02144	390	0.02122	335	0.02100	291	0.02078	255	0.02056	223
0.6	85	0.02625	295	0.02589	258	0.02553	230	0.02517	205	0.02481	186
0.7	85	0.03414	223	0.03354	198	0.03294	179	0.03234	163	0.03174	154
0.8	85	0.04897	161	0.04827	149	0.04757	138	0.04687	130	0.04617	121
0.1	95	0.01251	1430	0.01247	1150	0.01243	969	0.01239	817	0.01235	675
0.2	95	0.01397	985	0.01392	820	0.01387	702	0.01382	598	0.01377	504
0.3	95	0.01587	725	0.01580	620	0.01573	538	0.01566	462	0.01559	394
0.4	95	0.01837	555	0.01826	483	0.01815	421	0.01804	369	0.01793	322
0.5	95	0.02177	430	0.02155	380	0.02133	336	0.02111	301	0.02089	273
0.6	95	0.02666	335	0.02630	300	0.02594	271	0.02558	250	0.02522	231
0.7	95	0.03467	258	0.03407	236	0.03347	218	0.03287	203	0.03227	192
0.8	95	0.04973	195	0.04903	185	0.04833	175	0.04763	167	0.04693	159
0.1	105	0.01270	1470	0.01266	1207	0.01262	1037	0.01258	896	0.01254	765
0.2	105	0.01419	1040	0.01414	879	0.01409	767	0.01404	671	0.01399	585
0.3	105	0.01611	780	0.01604	681	0.01597	601	0.01590	530	0.01583	468
0.4	105	0.01865	607	0.01854	531	0.01843	475	0.01832	425	0.01821	384
0.5	105	0.02210	484	0.02188	433	0.02166	390	0.02144	358	0.02122	331
0.6	105	0.02707	384	0.02671	348	0.02635	322	0.02599	302	0.02563	285
0.7	105	0.03520	303	0.03460	281	0.03400	266	0.03340	254	0.03280	245
0.8	105	0.05049	235	0.04979	225	0.04909	217	0.04839	212	0.04769	207
0.1	115	0.01290	1518	0.01286	1279	0.01282	1117	0.01278	981	0.01274	856
0.2	115	0.01441	1115	0.01436	963	0.01431	853	0.01426	756	0.01421	669
0.3	115	0.01635	845	0.01628	760	0.01621	683	0.01614	613	0.01607	548
0.4	115	0.01893	668	0.01882	607	0.01871	555	0.01860	510	0.01849	468
0.5	115	0.02244	540	0.02222	499	0.02200	464	0.02178	435	0.02156	409
0.6	115	0.02747	435	0.02711	409	0.02674	388	0.02639	371	0.02603	359
0.7	115	0.03574	355	0.03514	338	0.03454	325	0.03394	318	0.03334	314
0.8	115	0.05125	285	0.05055	280	0.04985	275	0.04915	272	0.04845	269
0.1	125	0.01309	1595	0.01305	1353	0.01301	1198	0.01297	1071	0.01293	954
0.2	125	0.01463	1200	0.01458	1045	0.01453	939	0.01448	850	0.01443	768
0.3	125	0.01659	934	0.01652	839	0.01645	765	0.01638	702	0.01631	645
0.4	125	0.01921	751	0.01910	687	0.01899	637	0.01888	595	0.01877	561
0.5	125	0.02277	618	0.02255	578	0.02233	546	0.02211	520	0.02189	500
0.6	125	0.02788	510	0.02752	486	0.02716	468	0.02680	455	0.02644	445
0.7	125	0.03627	425	0.03567	409	0.03507	401	0.03447	400	0.03387	400
0.8	125	0.05201	350	0.05131	350	0.05061	350	0.04991	350	0.04921	350
0.1	135	0.01328	1695	0.01324	1438	0.01320	1290	0.01316	1176	0.01312	1075
0.2	135	0.01485	1292	0.01480	1147	0.01475	1048	0.01470	963	0.01465	887
0.3	135	0.01683	1022	0.01676	945	0.01669	878	0.01662	820	0.01655	769
0.4	135	0.01949	835	0.01938	790	0.01927	750	0.01916	714	0.01905	683
0.5	135	0.02310	700	0.02288	679	0.02266	656	0.02244	635	0.02222	612
0.6	135	0.02829	592	0.02793	583	0.02757	573	0.02721	563	0.02685	555
0.7	135	0.03680	505	0.03620	504	0.03560	501	0.03500	500	0.03440	500
0.8	135	0.05277	433	0.05207	430	0.05137	435	0.05067	441	0.04997	445
0.1	150	0.01357	1880	0.01353	1600	0.01349	1465	0.01345	1381	0.01341	1317
0.2	150	0.01517	1475	0.01512	1321	0.01507	1245	0.01502	1195	0.01497	1157
0.3	150	0.01719	1185	0.01712	1125	0.01705	1085	0.01698	1054	0.01691	1030
0.4	150	0.01991	988	0.01980	977	0.01969	962	0.01958	947	0.01947	932
0.5	150	0.02360	852	0.02338	865	0.02316	858	0.02294	850	0.02272	842
0.6	150	0.02890	755	0.02854	765	0.02818	765	0.02782	765	0.02746	765
0.7	150	0.03760	675	0.03700	667	0.03640	677	0.03580	687	0.03520	697
0.8	150	0.05391	602	0.05321	575	0.05251	593	0.05181	610	0.05111	626

tube, F (or C), corresponding to the exact volume of sample to be taken, was located by means of the cathetometer. A suitable cooling bath was brought up around the tube and the component was distilled from its respective storage bulb into the tube. When slightly more liquid than necessary had been transferred, the stopcock (E' or B') to the storage bulb and the stopcock (C' or F') on the volumetric tube were closed and stopcock J to trap K was opened. Then, the stopcock (C' or F') to the volumetric tube was reopened cautiously and the liquid was distilled at a slow rate to trap K until the meniscus was exactly on the cross

hairs of the cathetometer. Stopcock C' (or F') was then closed and the tube was kept at 0°C . while the required amount of the second component was measured in a similar manner, in the second volumetric tube.

At this stage in the procedure, the fluorolube oil in flask L was degassed by opening stopcock L' and pumping on the liquid until bubbles no longer formed, and the pressure, measured by the McLeod gage, was less than 1×10^{-5} mm. of mercury. During the pumping, the oil was agitated by rotating the flask rapidly through a 90° angle about the ground joint, I .

Table V. Phase Relations in Nitric Acid-Water System at Physicochemical Equilibrium

V^G/V	Temp., °C.	1.00 Weight % H ₂ O		2.00 Weight % H ₂ O		3.00 Weight % H ₂ O		4.00 Weight % H ₂ O		5.00 Weight % H ₂ O	
		Specific volume, cu. ft./ lb.	Equilibrium pressure, lb./sq. inch abs.	Specific volume, cu. ft./ lb.	Equilibrium pressure, lb./sq. inch abs.	Specific volume, cu. ft./ lb.	Equilibrium pressure, lb./sq. inch abs.	Specific volume, cu. ft./ lb.	Equilibrium pressure, lb./sq. inch abs.	Specific volume, cu. ft./ lb.	Equilibrium pressure, lb./sq. inch abs.
0.1	85	0.01239	1083	0.01246	873	0.01254	715	0.01261	584	0.01268	469
0.2	85	0.01383	732	0.01391	598	0.01399	495	0.01407	412	0.01415	338
0.3	85	0.01572	537	0.01581	440	0.01591	367	0.01600	310	0.01609	263
0.4	85	0.01820	405	0.01831	333	0.01840	280	0.01851	241	0.01863	212
0.5	85	0.02157	309	0.02170	255	0.02182	219	0.02195	193	0.02208	175
0.6	85	0.02641	236	0.02656	197	0.02672	171	0.02687	154	0.02703	142
0.7	85	0.03434	180	0.03454	151	0.03474	132	0.03495	120	0.03514	109
0.8	85	0.04926	134	0.04955	114	0.04983	95	0.05012	85	0.05041	80
0.1	95	0.01258	1118	0.01265	910	0.01272	751	0.01279	621	0.01287	507
0.2	95	0.01405	776	0.01413	639	0.01421	535	0.01429	448	0.01437	374
0.3	95	0.01596	580	0.01605	480	0.01615	405	0.01624	345	0.01633	295
0.4	95	0.01848	449	0.01859	375	0.01869	320	0.01880	276	0.01891	241
0.5	95	0.02190	345	0.02203	289	0.02215	249	0.02228	219	0.02241	196
0.6	95	0.02682	275	0.02697	235	0.02713	204	0.02728	180	0.02744	163
0.7	95	0.03487	210	0.03507	179	0.03527	157	0.03547	141	0.03567	129
0.8	95	0.05002	152	0.05031	125	0.05059	110	0.05088	104	0.05117	100
0.1	105	0.01277	1170	0.01284	974	0.01292	815	0.01299	677	0.01306	552
0.2	105	0.01427	838	0.01435	700	0.01443	591	0.01451	500	0.01459	420
0.3	105	0.01620	634	0.01629	534	0.01639	455	0.01648	392	0.01657	338
0.4	105	0.01876	500	0.01887	423	0.01897	365	0.01908	320	0.01919	280
0.5	105	0.02223	400	0.02236	340	0.02248	296	0.02261	263	0.02274	236
0.6	105	0.02723	318	0.02738	272	0.02754	240	0.02769	215	0.02785	198
0.7	105	0.03540	247	0.03560	210	0.03580	185	0.03600	171	0.03620	161
0.8	105	0.05078	186	0.05107	155	0.05135	140	0.05164	131	0.05193	128
0.1	115	0.01297	1235	0.01304	1033	0.01312	876	0.01319	741	0.01326	623
0.2	115	0.01449	912	0.01457	765	0.01465	652	0.01473	560	0.01481	482
0.3	115	0.01644	701	0.01653	596	0.01663	515	0.01672	448	0.01681	392
0.4	115	0.01904	560	0.01915	481	0.01925	420	0.01936	372	0.01947	333
0.5	115	0.02257	456	0.02270	395	0.02282	350	0.02295	314	0.02308	285
0.6	115	0.02763	370	0.02778	322	0.02794	287	0.02809	262	0.02825	241
0.7	115	0.03594	298	0.03614	260	0.03634	232	0.03654	214	0.03674	200
0.8	115	0.05154	235	0.05183	201	0.05211	180	0.05240	170	0.05269	162
0.1	125	0.01316	1310	0.01323	1109	0.01331	950	0.01338	815	0.01345	693
0.2	125	0.01471	994	0.01479	845	0.01487	730	0.01495	634	0.01503	551
0.3	125	0.01668	780	0.01677	670	0.01687	585	0.01696	516	0.01705	458
0.4	125	0.01932	632	0.01943	545	0.01953	481	0.01964	430	0.01975	388
0.5	125	0.02290	523	0.02303	456	0.02315	405	0.02328	366	0.02341	335
0.6	125	0.02804	433	0.02819	380	0.02835	340	0.02850	312	0.02866	290
0.7	125	0.03647	361	0.03667	318	0.03687	286	0.03707	265	0.03727	248
0.8	125	0.05230	295	0.05259	260	0.05287	235	0.05316	220	0.05345	210
0.1	135	0.01335	1403	0.01342	1199	0.01350	1038	0.01357	901	0.01364	779
0.2	135	0.01493	1085	0.01501	935	0.01509	818	0.01517	720	0.01525	636
0.3	135	0.01692	871	0.01701	760	0.01711	673	0.01720	601	0.01729	540
0.4	135	0.01960	719	0.01971	634	0.01981	566	0.01992	511	0.02003	465
0.5	135	0.02323	607	0.02336	540	0.02348	485	0.02361	442	0.02374	406
0.6	135	0.02845	517	0.02860	460	0.02876	417	0.02891	384	0.02907	355
0.7	135	0.03700	441	0.03720	394	0.03740	358	0.03760	331	0.03780	310
0.8	135	0.05306	374	0.05335	333	0.05363	303	0.05392	282	0.05421	267
0.1	150	0.01364	1580	0.01371	1372	0.01379	1210	0.01386	1075	0.01393	953
0.2	150	0.01525	1265	0.01533	1113	0.01541	993	0.01549	890	0.01557	800
0.3	150	0.01729	1038	0.01737	927	0.01747	836	0.01756	760	0.01765	695
0.4	150	0.02002	875	0.02013	790	0.02023	720	0.02034	664	0.02045	614
0.5	150	0.02373	758	0.02386	687	0.02398	630	0.02411	585	0.02424	545
0.6	150	0.02906	668	0.02921	605	0.02937	556	0.02952	517	0.02968	484
0.7	150	0.03780	596	0.03800	540	0.03820	495	0.03840	460	0.03860	430
0.8	150	0.05420	530	0.05449	476	0.05477	435	0.05506	405	0.05535	378

When the degassing operation was completed, stopcock L' was closed and the separate components were distilled in succession to the sample section of the experimental tube, G , which was held at liquid nitrogen temperature. To make certain that the transfer was complete, the system was allowed to stand for several hours after the last trace of liquid had disappeared from its volumetric tube. Careful measurements had previously shown that the liquid could be quantitatively transferred from the volumetric tube into the experimental tube and vice versa. Stopcock L' was then opened and by rotating flask L around ground joint I , fluoro-

lube was poured into the experimental tube. The tube was filled with the inert oil to a level just below mark H , on the experimental tube (Figure 2). The tube was then sealed off at H and the sample was kept frozen until the tube was introduced into the compressor block.

The order in which the components were transferred was important to the successful preparation of a mixture. For the nitric acid-water system it was found advisable to transfer part of the acid, then add the water and, finally, the remainder of the acid. The mixture was then melted, stirred by means of the magnetic stirrer (5), and refrozen. This

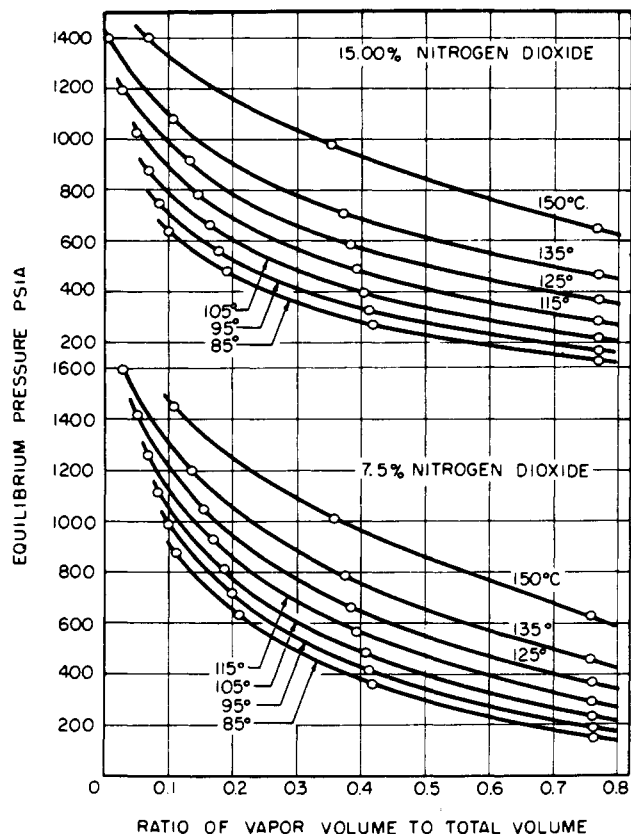


Figure 3. Relations between equilibrium pressure and V^G/V ratio for different temperatures in nitric acid-nitrogen dioxide system

procedure was necessary to prevent the freezing water from bursting the experimental tube. In the nitric acid-nitrogen dioxide system, the nitrogen dioxide was transferred first and the nitric acid was distilled on top of the frozen nitrogen dioxide.

By the method described, mixtures of any composition could be obtained to within 0.02 weight % and the specific volume to within 0.1% of the desired value.

APPARATUS AND PROCEDURE

In the measurement of the decomposition pressures of nitric acid-nitrogen dioxide and nitric acid-water mixtures, a sample, prepared as described, was maintained under isochoric conditions at a constant temperature and was stirred continuously until physicochemical equilibrium was reached, as indicated by the constancy of the pressure of the sample. The temperature was then changed and the experiment was repeated at the new temperature. The apparatus, the method of stirring the sample, and the procedure were the same as employed for similar measurements on initially pure nitric acid (5). The temperature of the sample was kept constant to within 0.05°C . and was measured by a calibrated mercury thermometer marked in 0.1°C . divisions. The pressure was indicated by a 0 to 2000 pound per square inch precision Bourdon-type gage with a 16-inch dial, hand-marked in 2-pound divisions. The gage was tested at 20-pound intervals with a precision dead weight gage tester. Pressures were read to 1.0 pound per square inch. The volume of the vapor phase of the sample was determined from the length of the tube occupied by the vapor, using a cathetometer for the measurement. From a knowledge of the vapor volume and the total volume of the sample section of the experimental tube, the V^G/V ratio was calculated. The accuracy was estimated to be within 0.001 of the true value of the ratio.

APPROACH TO PHYSICOCHEMICAL EQUILIBRIUM

The systems nitric acid-nitrogen dioxide and nitric acid-water were found to be unstable and to decompose in the concentration range and temperature range covered in the present work. As in the case of pure nitric acid (5), the decomposition of the mixtures investigated was completely reversible and the decomposition pressure was dependent only on temperature and the V^G/V ratio for a given initial composition.

Table I lists the time required to attain 90% of the equilibrium pressure at 85°C . and at selected V^G/V ratios when the sample was continuously stirred. This value, which characterizes the rate of decomposition, is decreased by the addition of nitrogen dioxide and increased by the addition of water or by an increase in the V^G/V ratio.

In the case of all nitric acid-nitrogen dioxide mixtures equilibrium was attained, as judged by the constancy of pressure, in a comparatively short time. However, in the case of nitric acid-water mixtures containing 5% of water and for large V^G/V ratios the rate of decomposition was reduced to the extent that physicochemical equilibrium was not attained even after 55 hours at 85°C . Under such circumstances, the pressure was recorded continuously as a function of time for a period of up to about 55 hours and large scale plots were prepared of pressure vs. the reciprocal of time. By extrapolation to infinite time, the value of the equilibrium pressure was obtained graphically. Such corrections, obtained by graphical extrapolation, averaged 0.5% of the equilibrium pressure for the water runs, the maximum correction being 5.0 pounds per square inch. The equilibrium at the high temperatures was attained much more rapidly.

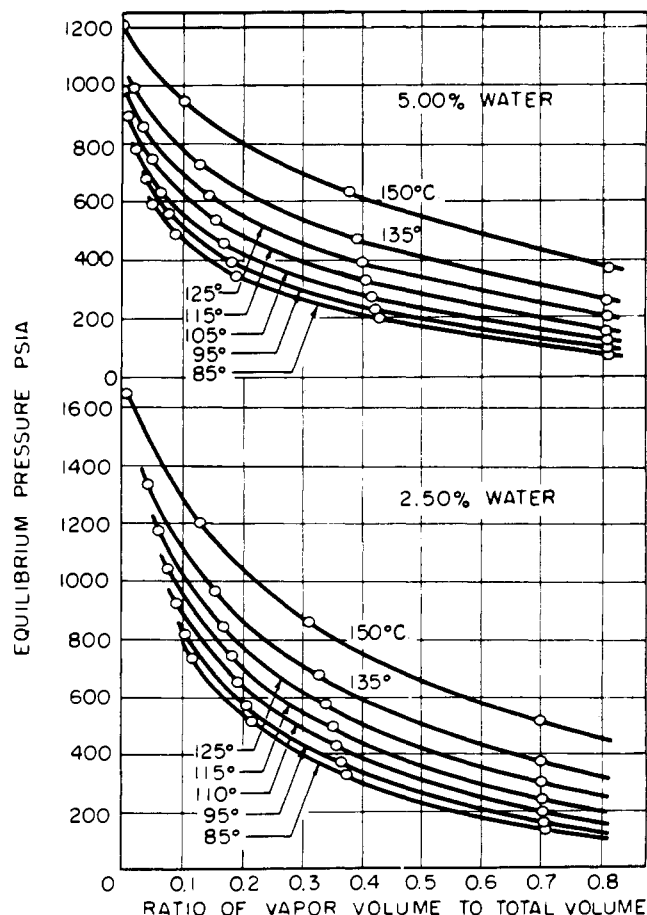


Figure 4. Relations between equilibrium pressure and V^G/V ratio for different temperatures in nitric acid-water system

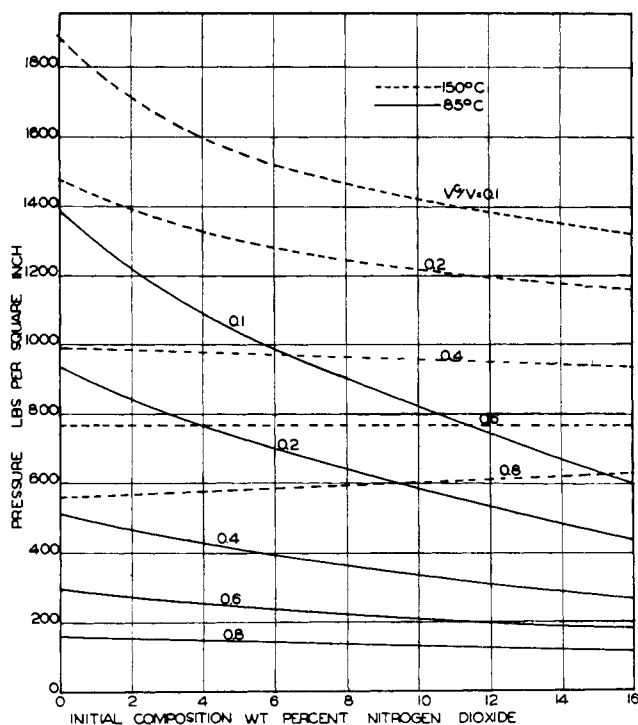


Figure 5. Relation among equilibrium pressure, initial composition, and V^G/V ratio at 85° and 150° C. in nitric acid-nitrogen dioxide system

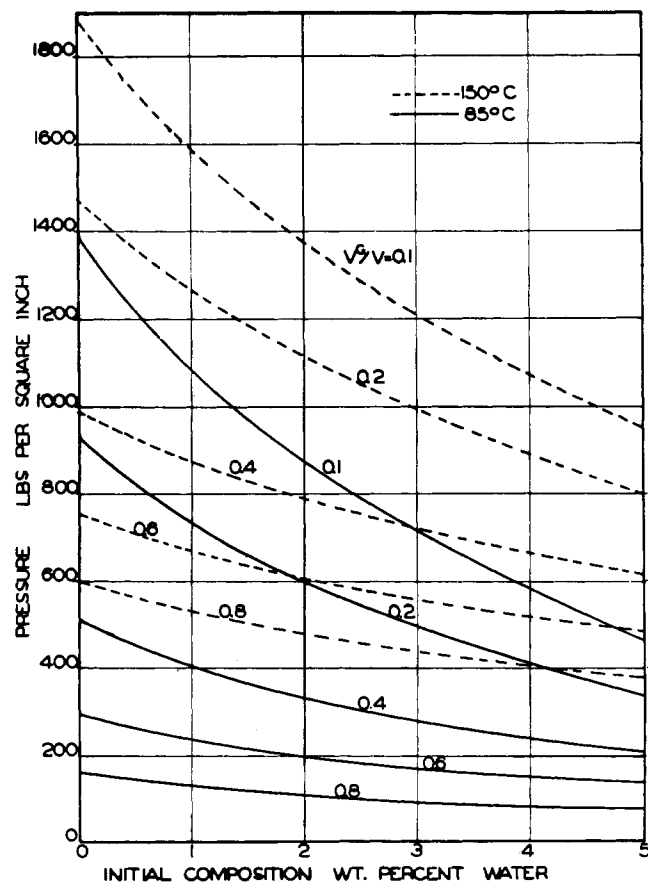


Figure 6. Relation among equilibrium pressure, initial composition, and V^G/V ratio at 85° and 150° C. in nitric acid-water system

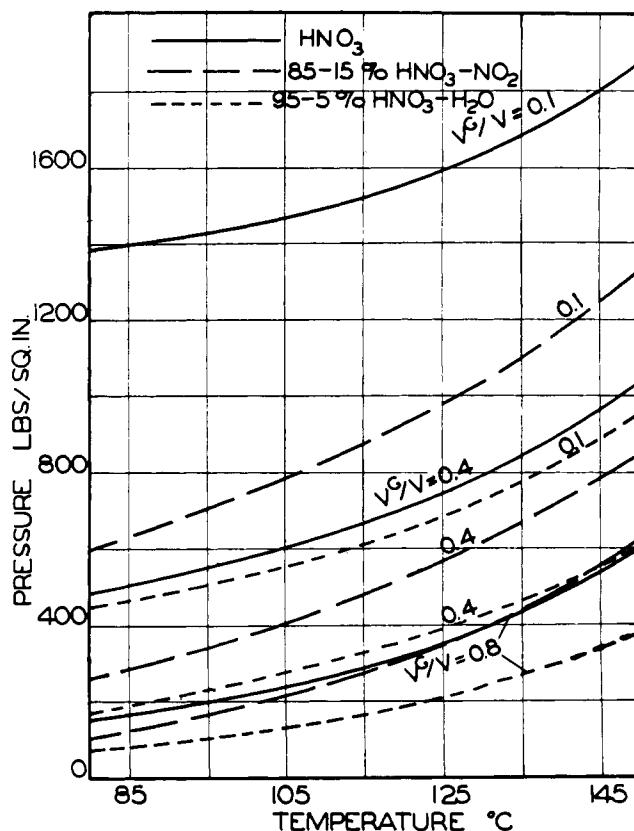


Figure 7. Comparison of equilibrium pressure-temperature- V^G/V relations of initially pure nitric acid and mixtures of nitric acid and nitrogen dioxide and nitric acid and water

VOLUMETRIC EQUILIBRIUM RELATIONS

Measurements of the equilibrium pressures of nitric acid-nitrogen dioxide mixtures containing initially 7.50 and 15.00 weight % of nitrogen dioxide and nitric acid-water mixtures containing initially 2.50 and 5.00 weight % of water were made at 85°, 95°, 105°, 115°, 125°, 135°, and 150°C., over a range of V^G/V ratios from approximately 0.8 to 0.05. The experimental data are presented in Tables II and III and are shown graphically in Figures 3 and 4 by a series of isothermal curves of equilibrium pressure vs. V^G/V ratio for the specified compositions. The data required to establish the curves for each composition were obtained by determining the equilibrium pressure under isochoric conditions of four samples of different specific volume at the stated temperatures. In every case the determinations were made in the order of increasing temperature, starting at 85°C. Upon completion of the measurement at 150°C., the pressure was redetermined at some lower temperature, in order to determine the loss, if any, of the sample due to its solution in the fluorolube oil, as would be indicated by a decrease in the value of the equilibrium pressure. If the decrease were greater than 1 pound per square inch, the indicated correction was made in the value of the equilibrium pressure. This correction never amounted to more than 1% of the total pressure under the most severe condition—namely, at 150°C.

The data have been interpolated by means of cross plots of the curves in Figures 3 and 4 and of supplementary plots of the specific volume as a function of the different variables. From these curves, drawn on an enlarged scale, values of the equilibrium pressure and of the corresponding specific volumes were read off at regular intervals of the V^G/V ratio at each of the seven stated temperatures, for

mixtures containing 4, 8, 12, and 16 weight % of nitrogen dioxide and 1, 2, 3, 4, and 5 weight % of water (Tables IV and V). The corresponding data for nitric acid (5) have been included for comparison.

The interpolation and subsequent smoothing have resulted in a small decrease in the accuracy of the tabulated data over that of the experimental. Nevertheless, the uncertainty in the values of the pressure given in the tables is believed to be less than 5 pounds per square inch or 1%, whichever is the larger value, at temperatures up to 125°C., and V^G/V ratios up to 0.6. The uncertainty may be somewhat larger at the higher temperatures and larger V^G/V ratios, particularly so, for the nitric acid-nitrogen dioxide mixtures.

Figure 5 shows graphically the relations between the equilibrium pressure and the amount of nitrogen dioxide initially present for different values of V^G/V at 85° and 150°C. The decrease in the equilibrium pressure with the amount of nitrogen dioxide added is greatest for small V^G/V ratios. At large V^G/V ratios, the relationship between the equilibrium pressure and the amount of nitrogen dioxide is essentially linear. The slope of these curves at large V^G/V ratios changes from negative to positive with increasing temperature. Between 105° and 125°C. (not shown on the graph) the equilibrium pressure is practically independent of the amount of nitrogen dioxide added. The increase in equilibrium pressure with the amount of nitrogen dioxide added at large V^G/V ratios and at the higher temperatures is indicative of an increase in the partial pressure of nitrogen dioxide relative to that of oxygen in the gas phase.

The relations between the equilibrium pressure and the

V^G/V ratio for the nitric acid-water mixtures studied are shown in Figure 6. The decrease in the equilibrium pressure with the amount of water added, on a weight basis, is considerably more pronounced than that obtained by the addition of nitrogen dioxide. However, this difference is much reduced if the comparison is made on a mole basis. The effects of V^G/V and temperature are about the same as for the nitric acid-nitrogen dioxide mixtures, except that the slopes of the curves are all negative for the range of concentration investigated.

Figure 7 shows a comparison of the relations between equilibrium pressure and temperature for pure nitric acid, for an 85 to 15% nitric acid-nitrogen dioxide mixture and for a 95 to 5% nitric acid-water mixture at V^G/V ratios of 0.1, 0.4, and 0.8. The curves demonstrate, in a striking manner, the very great dependence of the equilibrium pressure on the V^G/V ratio and the relatively greater effectiveness of water, as compared with nitrogen dioxide, in the reduction of the equilibrium pressure.

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Received for review March 22, 1956. Accepted June 19, 1956. Based on work performed under contract AF33(038)10381 with Wright Air Development Center, Wright-Patterson Air Force Base.

Vapor-Liquid Equilibria in Tetrahydrofuran-Methanol-Methyl Borate System

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Within the past few years, tetrahydrofuran (tetramethylene oxide) has become increasingly important as a commercial solvent, yet the chemical literature presents little information on the distillation behavior of systems containing tetrahydrofuran. Therefore, the present work was undertaken.

A preliminary investigation of the ternary system, tetrahydrofuran-methanol-methyl borate, gave no indication of the formation of a ternary azeotrope. Instead, it was found that upon fractionation of this system, two binary azeotropes which distill independently are obtained. In the presence of an excess of methanol, the well-known methanol-methyl borate azeotrope (3) distills at 54.6°C. until the methyl borate is exhausted. The temperature then rises to 59.1°C. and a methanol-tetrahydrofuran azeotrope distills.

As the behavior of the methanol-methyl borate system has previously been reported, only the two binary systems, methanol-tetrahydrofuran and methyl borate-tetrahydrofuran, are considered in this article.

EXPERIMENTAL

Materials. The tetrahydrofuran used was supplied by Du Pont and was distilled from sodium metal. Absolute methanol, supplied by J. T. Baker, was used without further purification. Methyl borate, obtained from Metal Hydrides, Inc., was distilled immediately before using.

Apparatus. The improved Othmer still (5) was used without modification to obtain equilibrium compositions. All distillations were carried out at atmospheric pressure, 740 to 750 mm. The thermometers used in this work were calibrated by observation of the ice point and by comparison with a thermocouple at several temperatures in the range of 0° to 60°C.

Analysis. The samples were analyzed by measuring the index of refraction with a Spencer Abbé refractometer and fitting these points to a previously determined curve of composition vs. index of refraction. For this work the refractometer was kept in a controlled-temperature room.

VAPOR-LIQUID EQUILIBRIUM DATA

The vapor-liquid equilibrium data for the two binary systems are shown in the Tables I and II and Figures 1 and 2. The graphs are the conventional $X - Y$ plots on which

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