Phase Relations in the Nitric Acid–Nitrogen Dioxide–Water System at Physicochemical Equilibrium

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In previous papers (*1, 2*), the phase relations of nitric acid and of binary mixtures of nitric acid and nitrogen dioxide and of nitric acid and water were presented. The range of concentration covered was up to 15 weight % of nitrogen dioxide and 5 weight % of water. It was found that the high physicochemical equilibrium pressure, observed in the case of nitric acid, is reduced considerably by the addition of either nitrogen dioxide or water. The work has been continued with a study of the phase relations of ternary mixtures of nitric acid, nitrogen dioxide, and water. A limited study has also been made of binary mixtures of nitric acid and nitric oxide. Measurements of the phase relations were made at temperatures between 85° and 150°C. and for the ratios of vapor volume to total volume, (V^G/V), from 0.8 to near zero, the bubble point of the mixture. The results are summarized in the present article.

Reamer, Corcoran, and Sage (*5*) have reported measurements on four compositions in the ternary system nitric acid-nitrogen dioxide-water, but their measurements were made primarily, in a region of lower specific volume than those covered in the present investigation.

PREPARATION OF MATERIALS

Nitric Acid. Nitric acid was prepared (*1*) by reaction of 100% sulfuric acid with anhydrous potassium nitrate at 0°C. in the complete absence of air, and the acid was collected as a solid at liquid nitrogen temperature. The acid showed, by chemical analysis, a total acidity of 99.98 ±0.05% HNO_3, with no trace of nitrogen dioxide or sulfur trioxide.

Nitrogen Dioxide. Nitrogen dioxide was prepared (*2*) by the thermal decomposition of pure, dry lead nitrate according to the equation

$$Pb(NO_3)_2(s) = PbO(s) + 2NO_2 + 1/2\ O_2\ (g) \qquad (1)$$

The gaseous nitrogen dioxide–oxygen mixture was dried over phosphorus pentoxide and subsequently the nitrogen dioxide was frozen out in a trap cooled with a dry ice–acetone mixture. The nitrogen dioxide was purified by contact in the liquid phase with oxygen gas to oxidize the lower oxides, and by repeated sublimation under high vacuum.

Nitric Oxide. Commercial nitric oxide gas having a

Table I. Experimental Data on Phase Relations in Nitric Acid–Nitrogen Dioxide–Water System at Physicochemical Equilibrium

(All pressures are in pounds per square inch absolute)

Initial Compn., Weight %			Molal Ratio, N_2O_4/H_2O	Spec. Vol., Cu. Ft./Lb.		Temperature, °C.						
HNO_3	NO_2	H_2O				85	95	105	115	125	135	150
90.00	0.00	10.00	0:1	0.01363	Press.	147	177	216	265	327	406	559
					V^G/V	0.149	0.138	0.125	0.114	0.101	0.088	0.064
70.00	30.00	0.00	1:0	0.01363	Press.	229	300	391	499	635	803	...
					V^G/V	0.217	0.204	0.187	0.169	0.148	0.121	...
94.70	4.69	0.61	1.5:1	0.01363	Press.	654	732	832	939	1076	1235	1540
					V^G/V	0.187	0.175	0.162	0.148	0.133	0.114	0.082
84.56	13.66	1.78	1.5:1	0.01363	Press.	178	231	307	395	509	...	...
					V^G/V	0.190	0.178	0.164	0.151	0.135	...	...
79.22	18.37	2.41	1.5:1	0.01363	Press.	82	122	177	245	340	461	721
					V^G/V	0.195	0.183	0.169	0.154	0.138	0.118	0.086
72.37	24.44	3.19	1.5:1	0.01363	Press.	80	113	160	217	294	396	...
					V^G/V	0.196	0.183	0.176	0.161	0.145	0.127	...
72.37	24.44	3.19	1.5:1	0.02371	Press.	79	111	158	212	287	...	...
					V^G/V	0.561	0.557	0.549	0.543	0.537	...	...
86.05	11.71	2.24	1:1	0.01363	Press.	176	218	299	384	494	627	...
					V^G/V	0.185	0.174	0.161	0.147	0.132	0.115	...
81.29	15.65	3.06	1:1	0.01363	Press.	78	114	165	228	315	428	655
					V^G/V	0.186	0.175	0.161	0.147	0.132	0.115	0.084
76.61	19.56	3.83	1:1	0.01363	Press.	72	105	147	200	272	...	...
					V^G/V	0.205	0.193	0.180	0.166	0.151	...	...
95.00	3.59	1.41	0.5:1	0.01363	Press.	580	653	746	851	969	...	...
					V^G/V	0.182	0.169	0.156	0.142	0.128	...	...
95.00	3.59	1.41	0.5:1	0.01762	Press.	340	389	450	522	615	728	942
					V^G/V	0.375	0.368	0.359	0.350	0.340	0.329	0.312
95.00	3.59	1.41	0.5:1	0.02389	Press.	232	272	323	385	458	...	...
					V^G/V	0.538	0.533	0.527	0.521	0.516	...	...
90.00	7.18	2.82	0.5:1	0.01363	Press.	222	270	343	418	520	644	884
					V^G/V	0.194	0.181	0.171	0.156	0.142	0.128	0.100
90.00	7.18	2.82	0.5:1	0.02371	Press.	134	170	217	275	348	...	...
					V^G/V	0.535	0.529	0.524	0.518	0.513	...	...
85.00	10.77	4.23	0.5:1	0.01363	Press.	80	114	161	221	302	407	616
					V^G/V	0.176	0.166	0.153	0.140	0.124	0.108	0.081
85.00	10.77	4.23	0.5:1	0.02371	Press.	70	99	138	190	256	...	...
					V^G/V	0.533	0.526	0.522	0.515	0.509	...	...
80.00	14.36	5.64	0.5:1	0.01363	Press.	58	84	118	168	232	...	...
					V^G/V	0.178	0.167	0.153	0.140	0.125	...	...

purity of 98.0% or better was admitted to a purification train from which all air had been removed and was passed, first through a trap cooled by dry ice and acetone, then through a drying tube 5 feet long, packed loosely with glass wool upon which phosphorus pentoxide was suspended, and finally was condensed and frozen in a trap cooled with liquid nitrogen. The solid was pumped for 10 to 15 minutes, then sublimed under a pressure of about 50 mm. of mercury and pumped again. This was repeated four times. The solid was stored at liquid nitrogen temperature until used.

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

PREPARATION OF MIXTURES

Ternary Mixtures of Nitric Acid-Nitrogen Dioxide-Water. Samples of ternary mixtures of nitric acid-nitrogen dioxide and water for the study of their phase relations were prepared by measuring each component separately in an apparatus free from any trace of air, and then transferring these quantities by distillation to the experimental tube to make a mixture of known composition. The apparatus and procedure were similar to those described for the preparation of binary mixtures of nitric acid-nitrogen dioxide and nitric acid-water (*2*). Mixtures of any composition to within 0.02 weight %, and of any specific volume to within 0.1 % could be prepared.

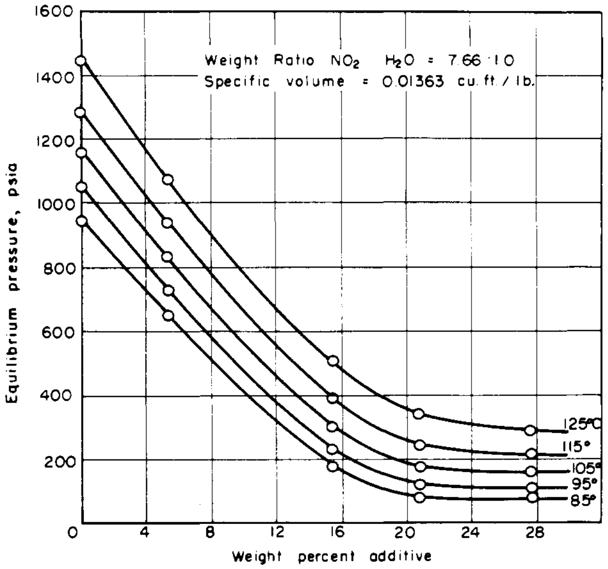


Figure 1. Relation between equilibrium pressure and composition at constant specific volume (0.01363 cu. ft./lb.) for ternary mixtures containing NO_2 and H_2O in proportion of 7.66 to 1 by weight

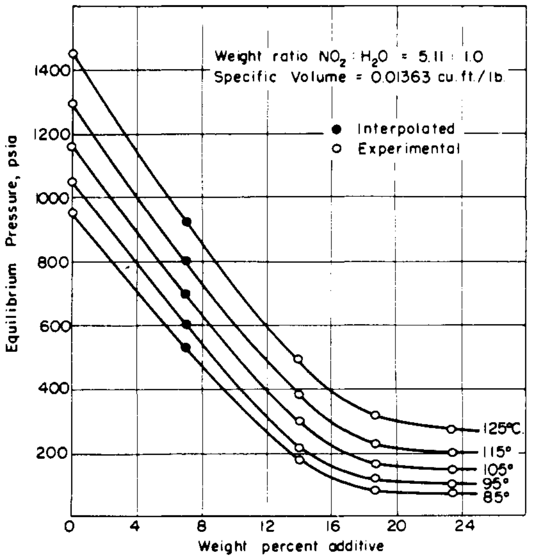


Figure 2. Relation between equilibrium pressure and composition at constant specific volume (0.01363 cu. ft./lb.) for ternary mixtures containing NO_2 and H_2O in the proportion of 5.11 to 1 by weight

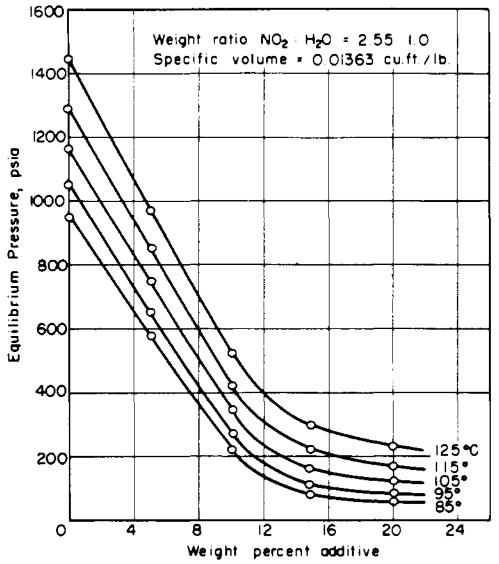


Figure 3. Relation between equilibrium pressure and composition at constant specific volume (0.01363 cu. ft./lb.) for ternary mixtures containing NO_2 and H_2O in proportion of 2.55 to 1 by weight

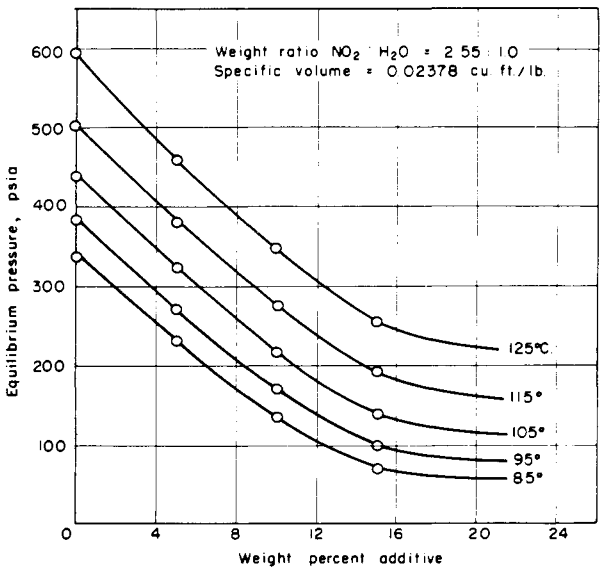


Figure 4. Relation between equilibrium pressure and composition at constant specific volume (0.02378 cu. ft./lb.) for ternary mixtures containing NO_2 and H_2O in proportion of 2.55 to 1 by weight

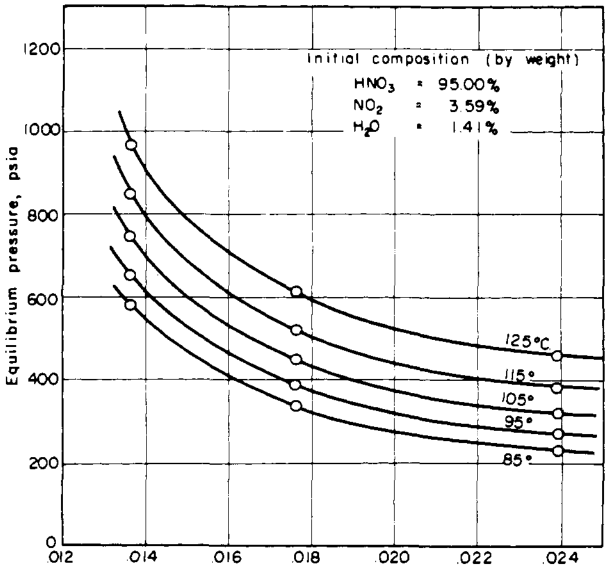


Figure 5. Relations between equilibrium pressure and V^G/V ratio at different temperatures for ternary mixtures containing initially 95.00% HNO_3, 3.59% NO_2, and 1.41% H_2O

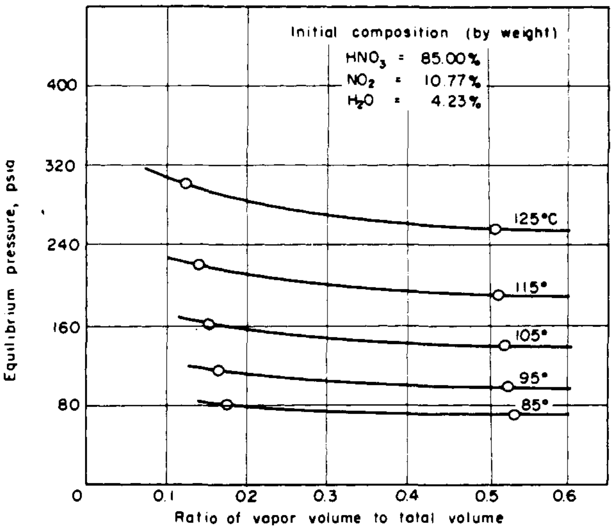


Figure 6. Relations between equilibrium pressure and V^G/V ratio at different temperatures for ternary mixtures containing 85.00% HNO_3, 10.77% NO_2, and 4.23% H_2O

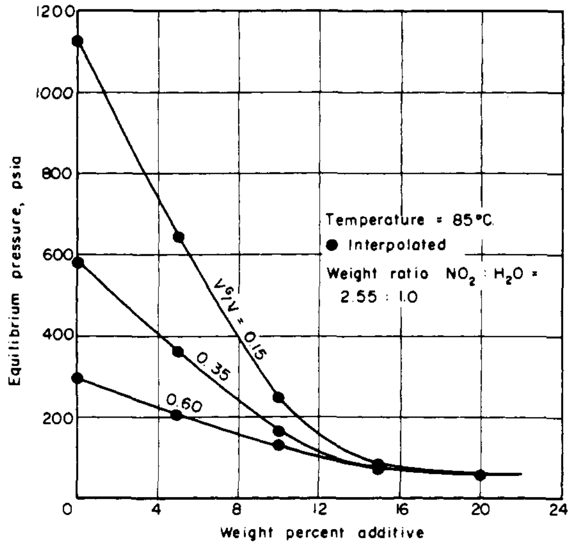


Figure 7. Relations between equilibrium pressure and initial composition for various values of V^G/V at 85°C. for ternary mixtures containing NO_2 and H_2O in proportion of 2.55 to 1 by weight

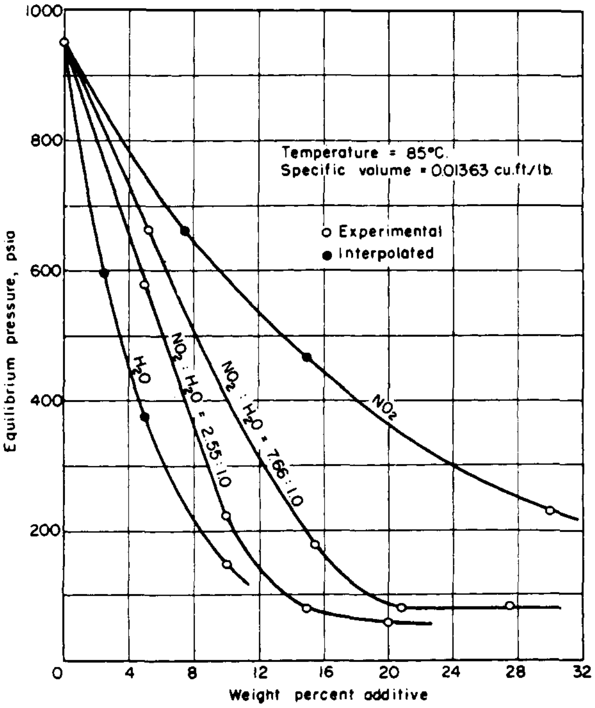


Figure 8. Comparison of effect of adding NO_2 and H_2O in various proportions to HNO_3 on equilibrium pressure at 85°C. in the HNO_3-NO_2-H_2O system

Mixtures of Nitric Acid and Nitric Oxide. A mixture of known composition of nitric acid and nitric oxide was prepared by transferring a measured amount of nitric acid to the experimental tube, then condensing a measured amount of the nitric oxide on top of the acid. The nitric oxide was measured by confining a sample of the gas at constant temperature and under a known pressure, in a bulb of known volume. The volumetric bulb was sealed directly to the trap in which the nitric oxide was stored. Attached to a side arm of the bulb was a mercury manometer.

To prepare a mixture of given specific volume and given composition, the pressure of the nitric oxide gas in the bulb, necessary to give the desired amount of nitric oxide, was computed for a reference temperature of 0°C. by means of the perfect gas law, and the cross hairs of the cathetometer were set accordingly on the manometer. The gas was then admitted to the bulb which was maintained at 0°C. by an ice bath, until the pressure was slightly greater than that computed. A stopcock on top of the volumetric bulb was then opened cautiously, and the gas was pumped off until the mercury level in the manometer coincided exactly with the cross hairs of the cathetometer. The remainder of the procedure was exactly the same as employed in the studies of binary and ternary mixtures of nitric acid, nitrogen dioxide, and water. It is estimated that the composition of the prepared mixture was known to within 0.01%.

APPARATUS AND PROCEDURE

For the measurement of the equilibrium pressure of nitric acid-nitrogen dioxide-water mixtures, a sample, prepared as described, was maintained under isochoric conditions at a constant temperature and was stirred continuously with a magnetic stirrer until physicochemical equilibrium was reached, as indicated by the constancy of the pressure exerted by the sample. The temperature was then changed and the experiment was repeated at the new temperature. The apparatus and procedure were the same as for similar measurements on initially pure nitric acid (2).

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 p.s.i. 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, the length having been related to the volume by a previous calibration of the tube. A cathetometer reading to 0.05 mm. was used for measurement of the length. From a knowledge of the vapor volume and the total volume of the

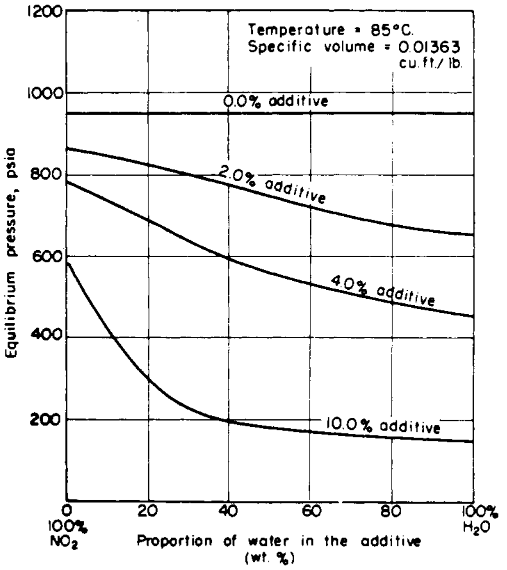
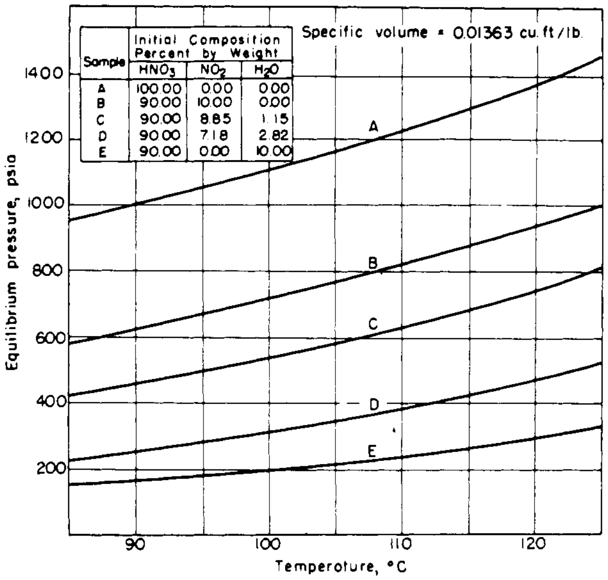


Figure 9. Relation between equilibrium pressure and proportion of water in the additive at 85°C. in the HNO_3-NO_2-H_2O system



Sample	Initial Composition Percent by Weight		
	HNO_3	NO_2	H_2O
A	100.00	0.00	0.00
B	90.00	10.00	0.00
C	90.00	8.85	1.15
D	90.00	7.18	2.82
E	90.00	0.00	10.00

Figure 10. Comparison of effect of adding NO_2 and H_2O in different proportions on the equilibrium pressure of the mixture at various temperatures in the HNO_3-NO_2-H_2O system

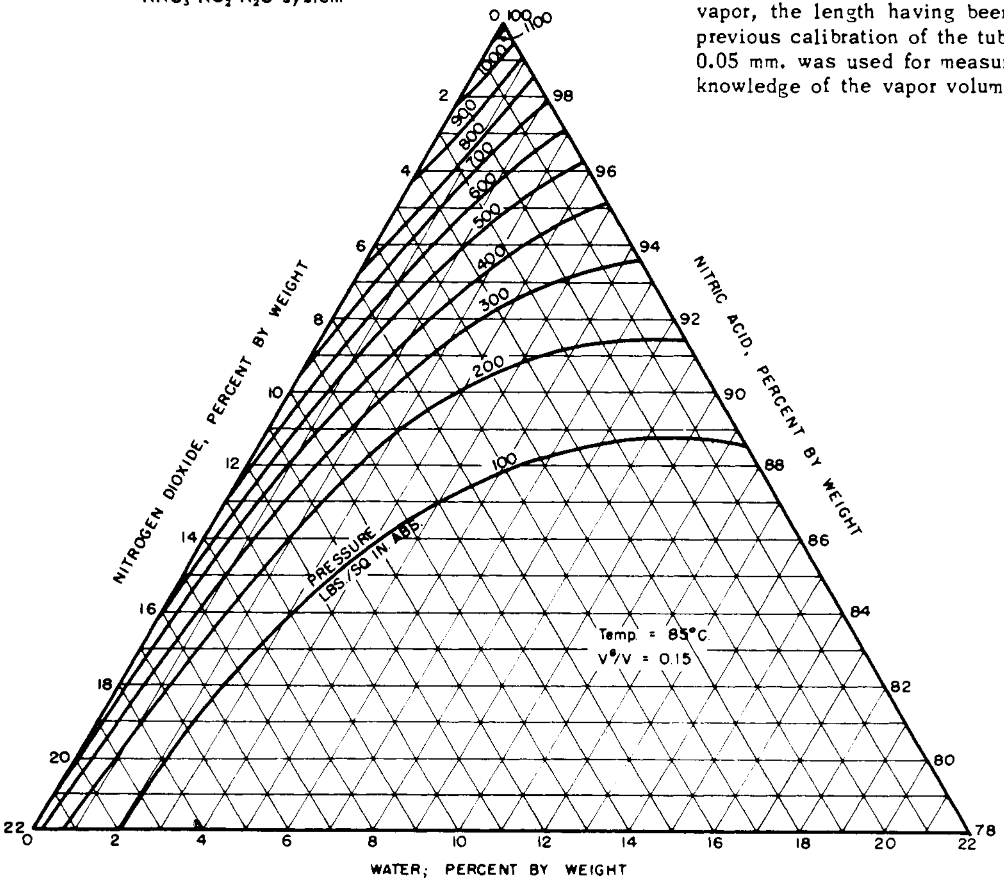


Figure 11. Equilibrium pressures in the nitric acid–nitrogen dioxide–water system

Temperature = 85°C., V^G/V = 0.15

sample section of the experimental tube, the V^G/V ratio was calculated. The accuracy was estimated to be within 0.1% of the true value of the ratio.

As in the case of the binary mixtures, the time required to reach equilibrium at a given temperature, as judged by the constancy of pressure, was dependent on the initial composition and the V^G/V ratio. Equilibrium was approached rapidly for all mixtures except those of nitric acid and water containing 10% of water. For the latter, equilibrium was not attained even after 45 hours at 85° C. In this case, the pressure was recorded as a function of time and a large scale plot was prepared of the pressure versus the reciprocal of time. By extrapolation to infinite time, the value of the equilibrium pressure was obtained graphically. Equilibrium at higher temperatures was attained much more rapidly.

RESULTS

To establish the relations among pressure, volume, temperature, and initial composition in the nitric acid-nitrogen dioxide-water system, in the region of high concentration of nitric acid, a total of 11 compositions associated with three restricted ternary systems containing nitrogen dioxide and water in the ratio of 7.66 : 1.0, 5.11 : 1.0, and 2.55 : 1.0, were studied. In addition, one composition each of the binary systems nitric acid-nitrogen dioxide and nitric acid-water was studied in order to extend the range of binary mixtures already investigated (*2*). Three mixtures of nitric acid with nitric oxide were also studied. The range of concentration covered was from 70 to 97.5% of nitric acid, 0 to 30% of nitrogen dioxide, 0 to 10% of water, and 0 to 3% of nitric oxide. Because for each experimental run the specific volume and the V^G/V ratio were fixed, it was necessary to study several mixtures of the same composition in order to determine the relation of these variables with the equilibrium pressure. For each of the mixtures the equilibrium pressures and V^G/V ratios were determined under isochoric conditions at 10°C. intervals from 85° to 125°C. and in some cases at 135° and 150°C. The experimental data are presented in Table I and shown graphically in Figures 1 through 4.

VOLUMETRIC EQUILIBRIUM RELATIONS

The isothermal relations between the equilibrium pressure and the initial composition for the three restricted ternary systems are shown in Figures 1 through 4. The composition has been expressed as the weight per cent of the additive, which is defined as the sum of the weight per cents of nitrogen dioxide and water in the mixture. The data points at 5.30 and 15.40% of the additive in Figure 1 were obtained from measurements on mixtures prepared by adding nitric oxide to nitric acid. Nitric oxide reacts with nitric acid according to the equation

$$2\ HNO_3 + NO = 3\ NO_2 + H_2O \qquad (2)$$

to give nitrogen dioxide and water in the weight ratio of 7.66 to 1. Mixtures so prepared were found to have the same properties as if the nitrogen dioxide and water in the same amounts had been added directly to the acid.

Figures 5 and 6 exhibit the effect of the V^G/V ratio on the equilibrium pressure when the temperature and initial composition are held constant. Figure 7 shows the relation between equilibrium pressure and weight per cent of additive with V^G/V as the parameter.

The relations depicted by the curves in Figures 1 through 7 are similar to those for the binary mixtures of HNO_3-NO_2 and HNO_3-H_2O (*2*). The equilibrium pressure is markedly decreased by the addition of nitrogen dioxide and water and reaches a minimum value between 20 and 28 weight % of the additive, depending on the temperature and the ratio of

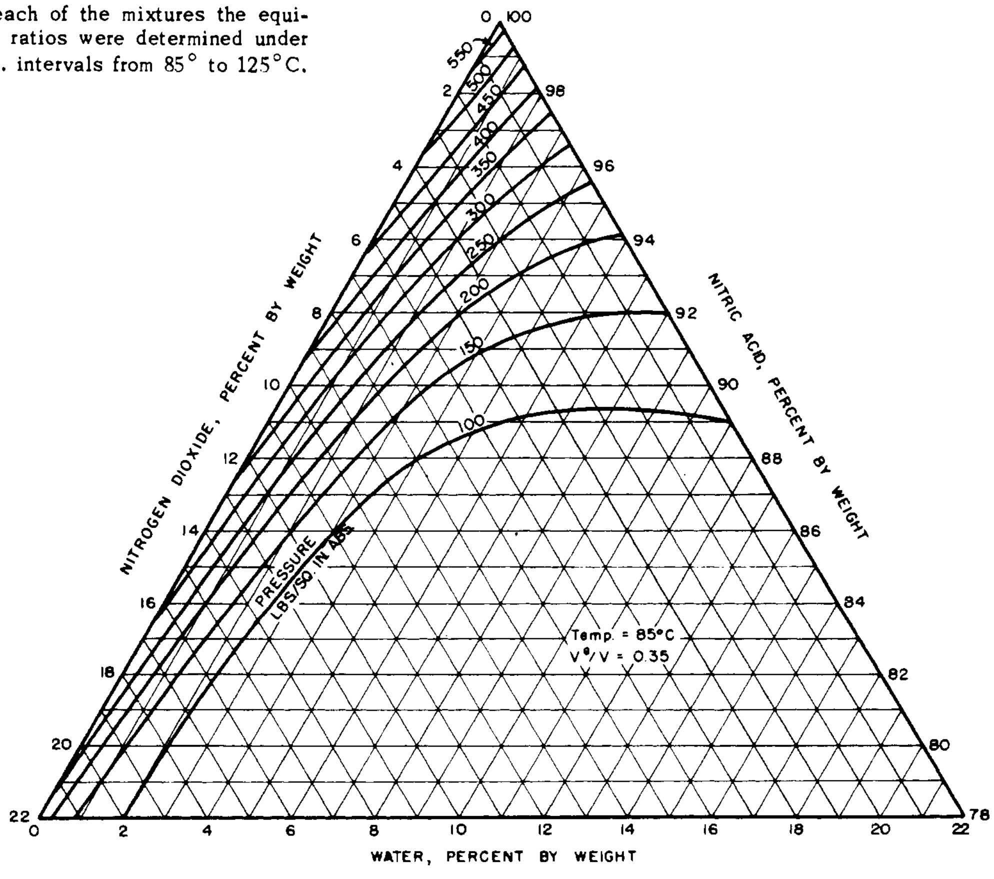


Figure 12. Equilibrium pressures in the nitric acid-nitrogen dioxide-water system

Temperature = 85°C., $V^G/V = 0.35$

nitrogen dioxide to water. A comparison of the curves in Figures 1, 2, and 3 indicates that, on the basis of equal amounts of the additive, the mixtures containing the greater amounts of water exhibit the lower equilibrium pressure. This difference between nitrogen dioxide and water, in their effectiveness to reduce the equilibrium pressure, is brought out by the curves in Figures 8 and 9. Figure 10 indicates that the same relations hold at higher temperatures. As in the case of the binaries, the equilibrium pressures of mixtures of high acid content are sensitive to the V^G/V ratio, but this sensitivity diminishes with a decrease in acid content and becomes insignificant below about 80% of nitric acid at 85°C. At higher temperature, this concentration will be somewhat less than 80%.

CORRELATION OF EXPERIMENTAL DATA

The relations among the equilibrium pressure, initial composition, V^G/V ratio, and temperature, exemplified by the curves in Figures 1 through 10, have been correlated and are expressed graphically by the triangular diagrams of Figures 11 through 22. Each triangular diagram shows the isobaric curves of the equilibrium pressure at regular pressure intervals, in their relation to the initial composition at a given temperature and V^G/V ratio.

Diagrams were prepared for the temperatures 85°, 105°, 125°, and 150°C. for each of the V^G/V ratios 0.15, 0.35, and 0.60.

The specific volumes of the heterogeneous mixtures in cubic feet per pound for the conditions stated in Figures 11 through 22 were correlated with the initial composition by the generalized empirical chart (Figure 23). To determine the specific volume of a mixture of any given initial composition, the value of the specific volume of the equilibrium mixture, resulting from the dissociation of pure nitric acid at the same temperature and V^G/V ratio, is multiplied by the composition factor read from the generalized chart (Figure 23). The specific volume of the equilibrium mixture for pure nitric acid to be used in the calculation, is given in Table II. The generalized chart is based on the assumption that lines of constant liquid density at 25°C. for the nitric acid–nitrogen dioxide–water system are also lines of constant specific volume of the heterogeneous sample at a given temperature and V^G/V ratio. The curves were constructed using the experimental data given in Table I and the density data of Stern and Kay (7), Klemenc and Rupp (3), Sprague and Kaufman (6), and Mason, Petker, and Vango (4). This method of estimating the equilibrium specific volume, when applied to the mixtures listed in Table I, gave values which agreed to within 1% of the experimental values.

Table II. Relation among V^G/V, Temperature, and Specific Volume for Initially Pure Nitric Acid at Physicochemical Equilibrium

	Specific Volume, Cu. Ft./Lb.		
Temp., °C.	$V^G/V = 0.15$	$V^G/V = 0.35$	$V^G/V = 0.60$
85	0.01300	0.01678	0.02625
105	0.01341	0.01729	0.02707
125	0.01382	0.01781	0.02788
150	0.01433	0.01845	0.02890

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(*Literature Cited on page 32*)

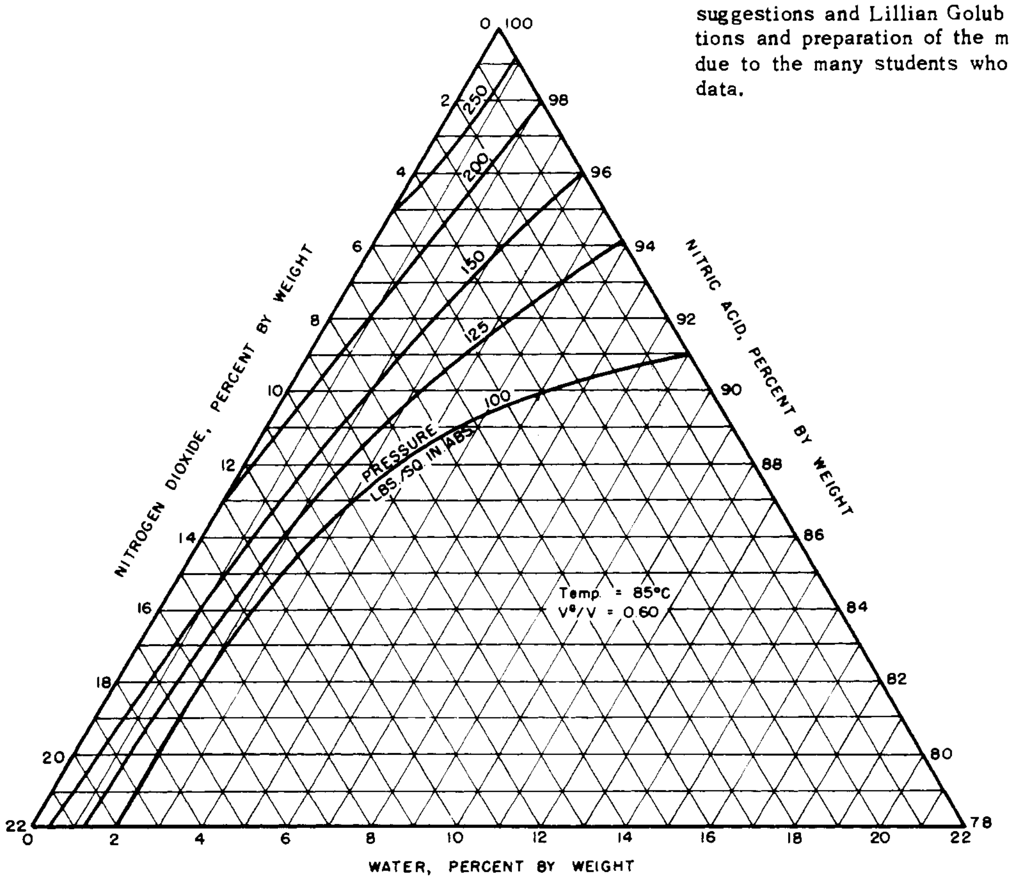


Figure 13. Equilibrium pressures in the nitric acid–nitrogen dioxide–water system

Temperature = 85°C., V^G/V = 0.60

Figure 14. Equilibrium pressures in the nitric acid–nitrogen dioxide–water system

Temperature = 105 °C., $V^G/V = 0.15$

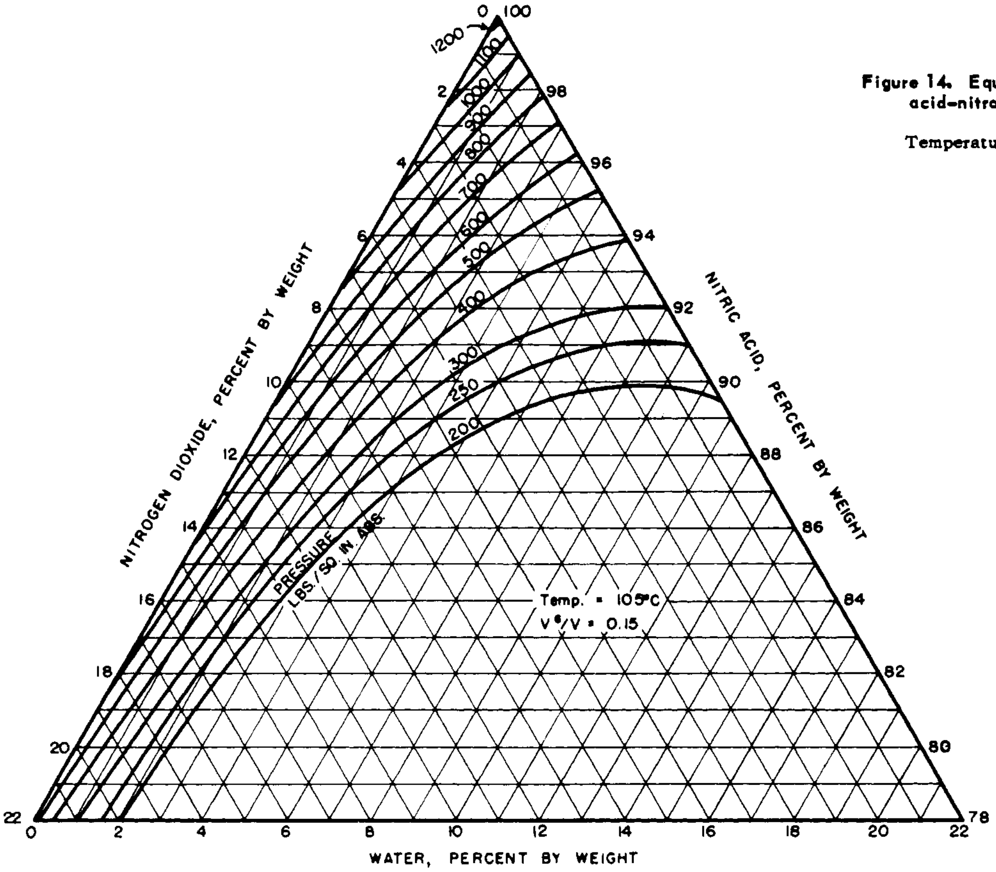


Figure 15. Equilibrium pressures in the nitic acid–nitrogen dioxide–water system

Temperature = 105 °C., $V^G/V = 0.35$

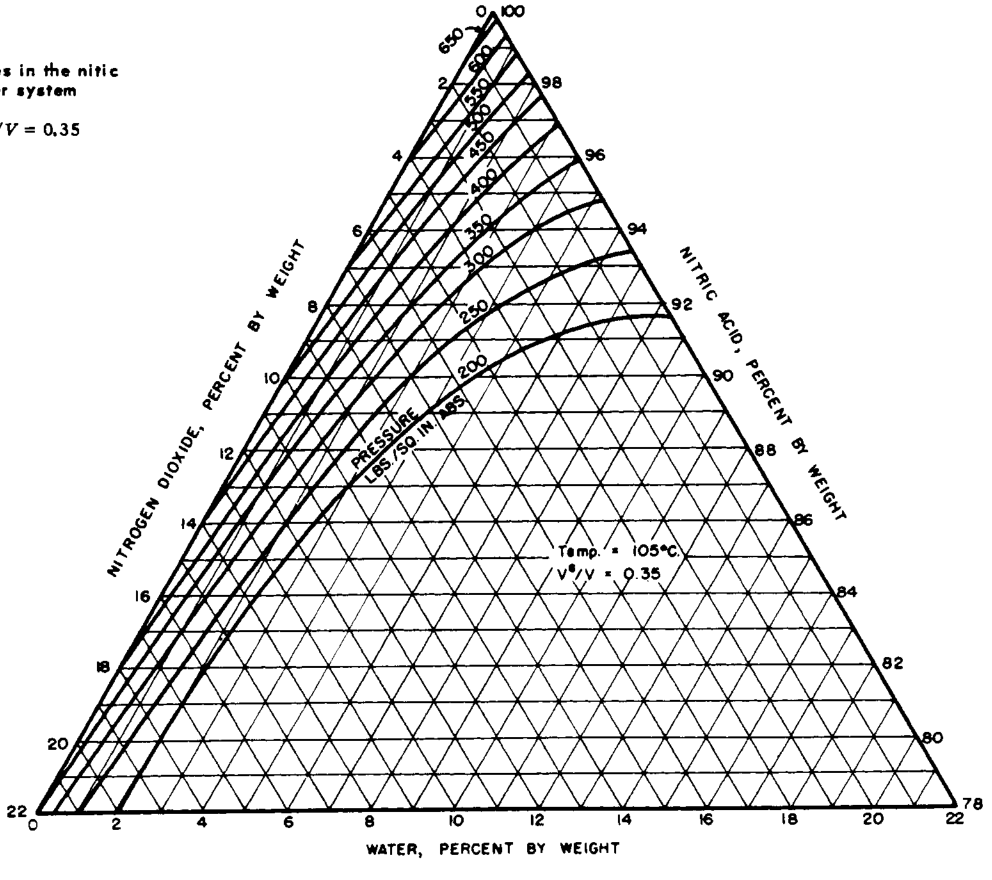


Figure 16. Equilibrium pressures in the nitric acid–nitrogen dioxide–water system

Temperature = 105 °C., $V^G/V = 0.60$

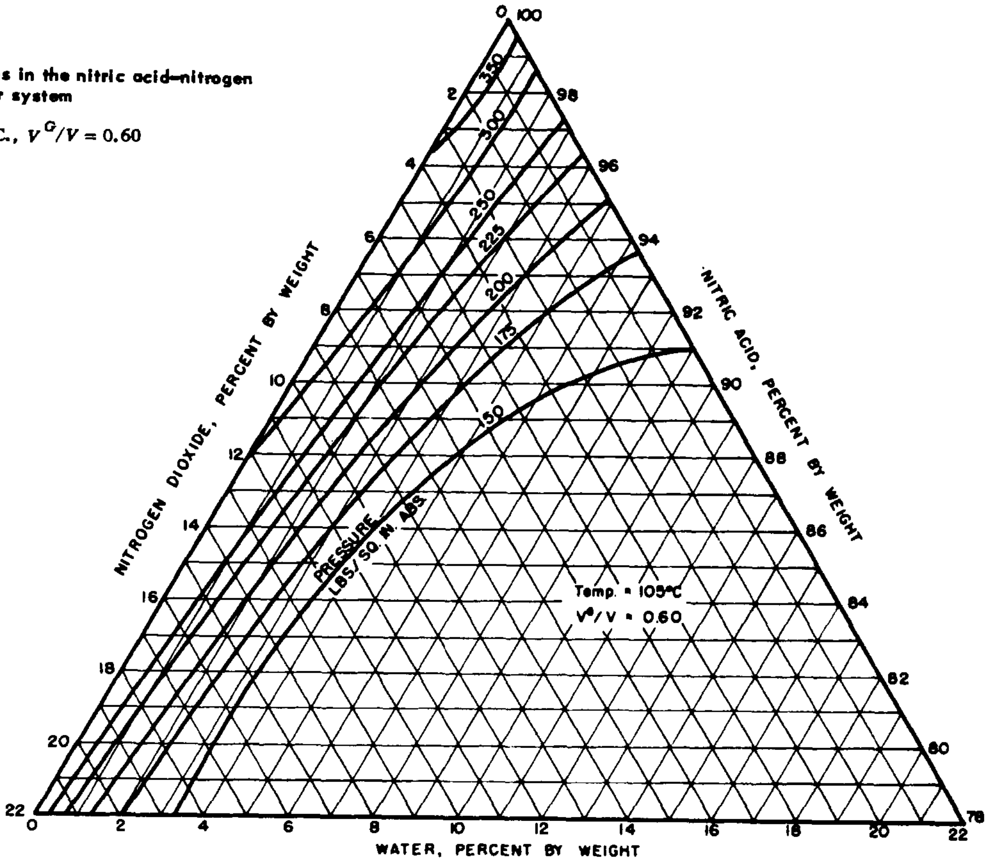
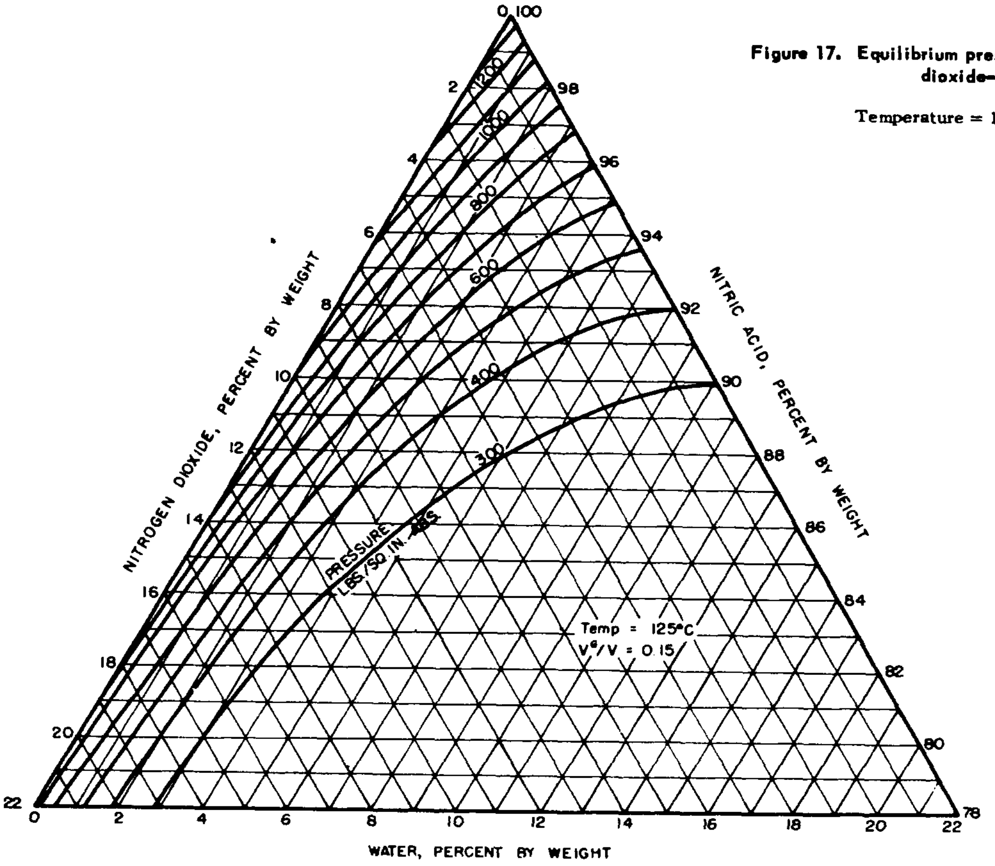


Figure 17. Equilibrium pressures in the nitric acid–nitrogen dioxide–water system

Temperature = 125 °C., $V^G/V = 0.15$



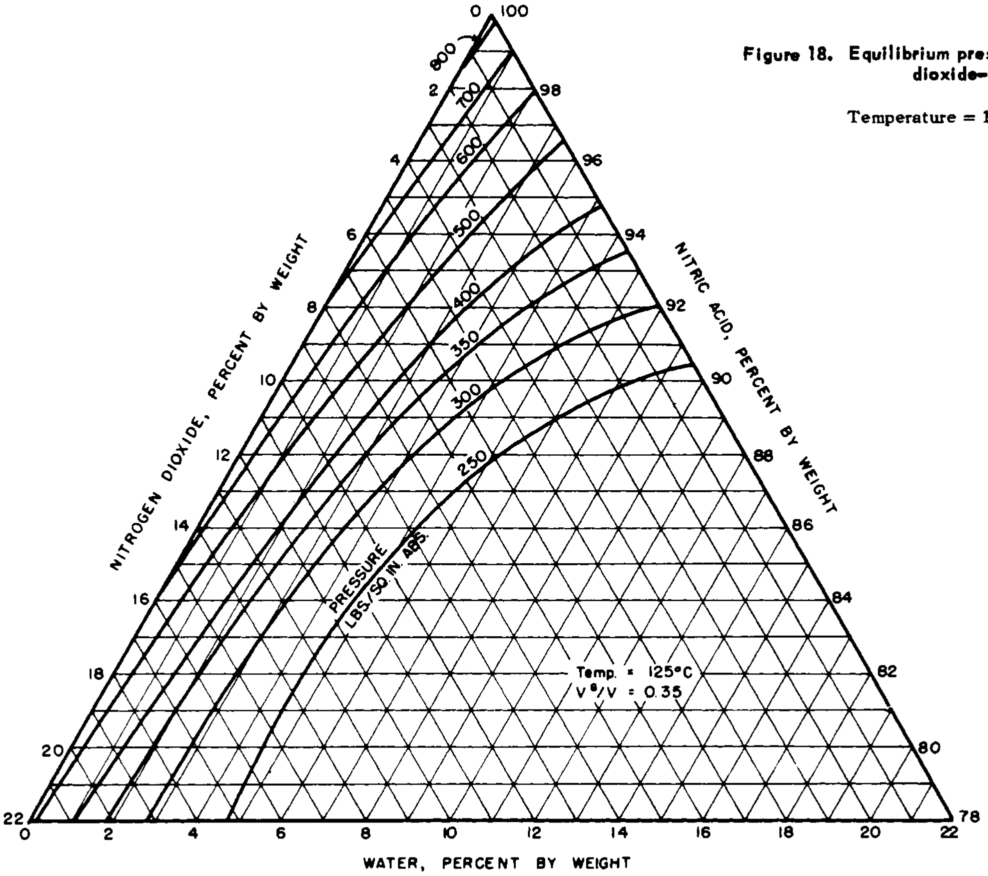
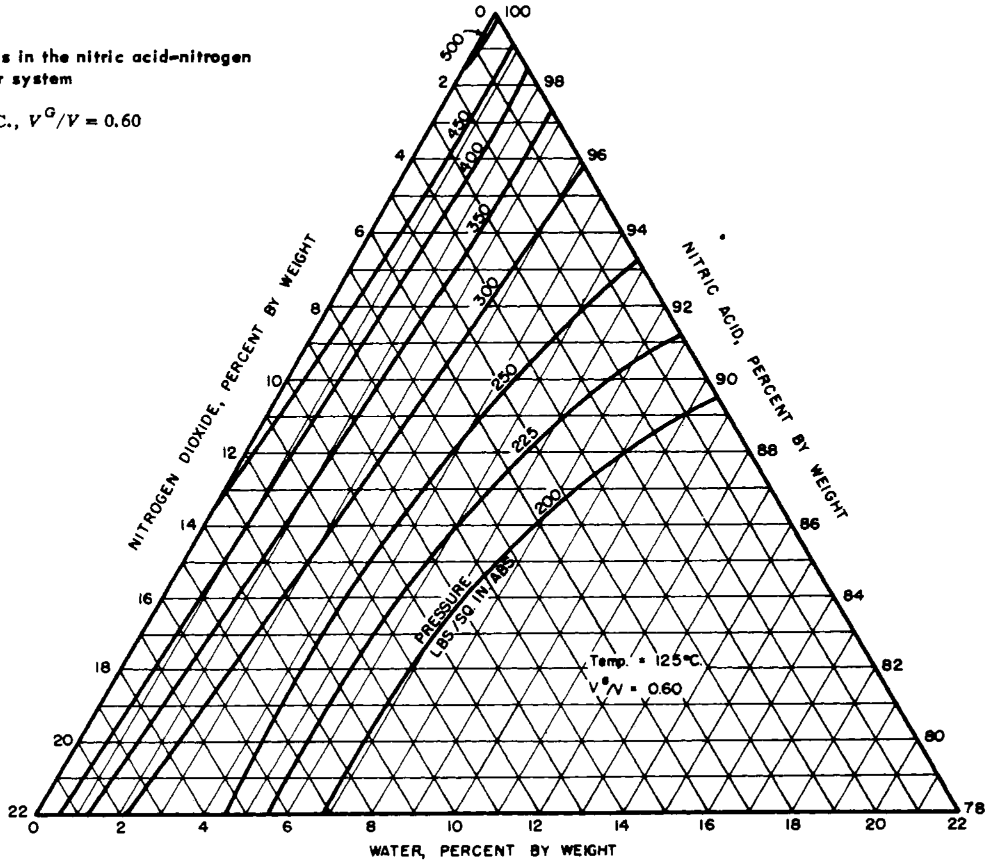


Figure 18. Equilibrium pressures in the nitric acid–nitrogen dioxide–water system

Temperature = 125°C., $V^G/V = 0.35$

Figure 19. Equilibrium pressures in the nitric acid–nitrogen dioxide–water system

Temperature = 125°C., $V^G/V = 0.60$



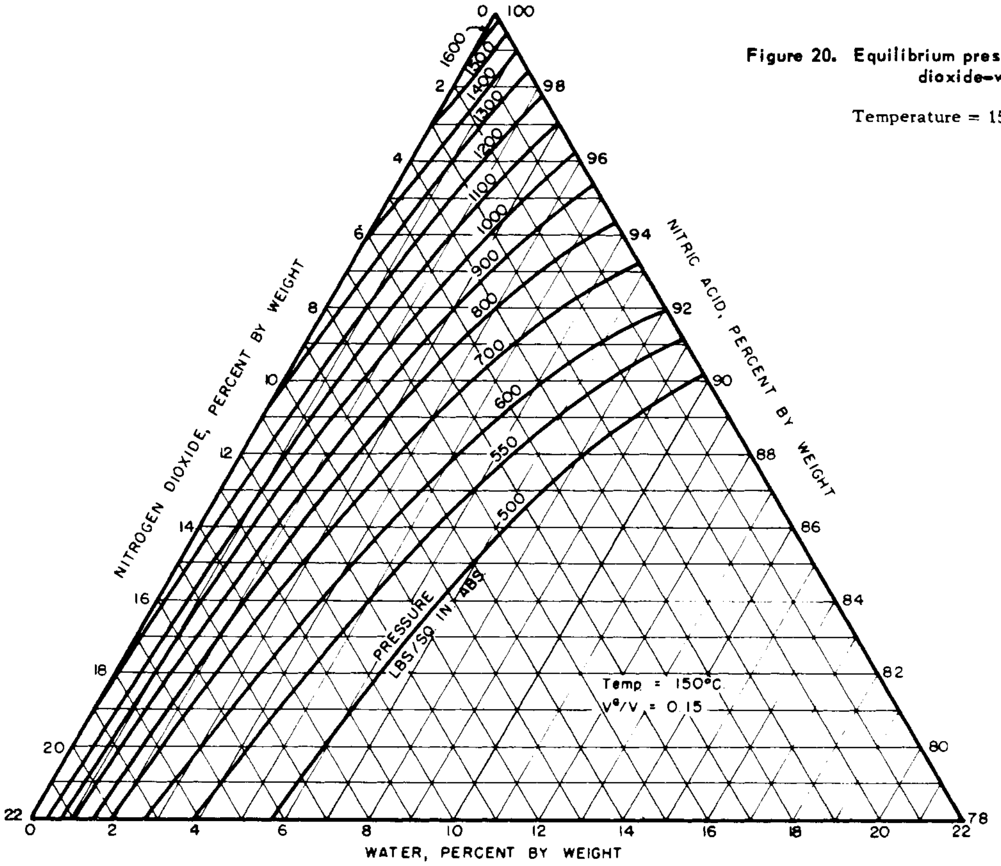


Figure 20. Equilibrium pressures in the nitric acid-nitrogen dioxide-water system

Temperature = 150°C., $V^G/V = 0.15$

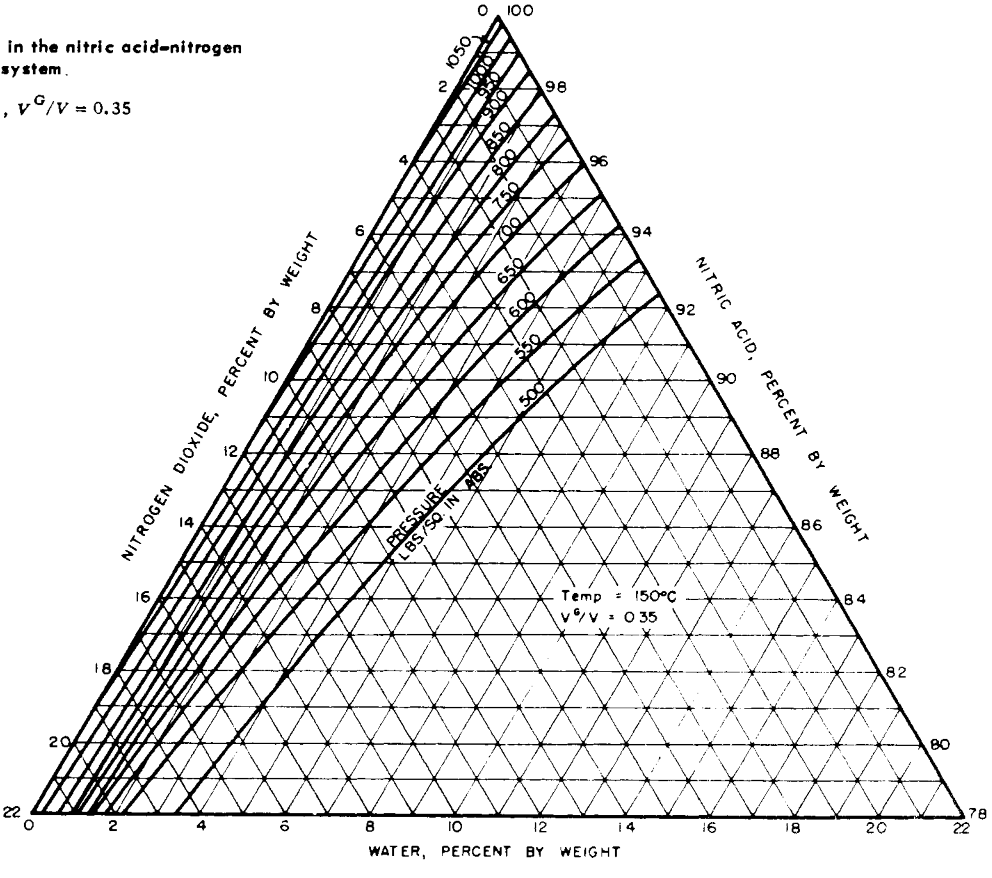


Figure 21. Equilibrium pressures in the nitric acid-nitrogen dioxide-water system.

Temperature = 150°C., $V^G/V = 0.35$

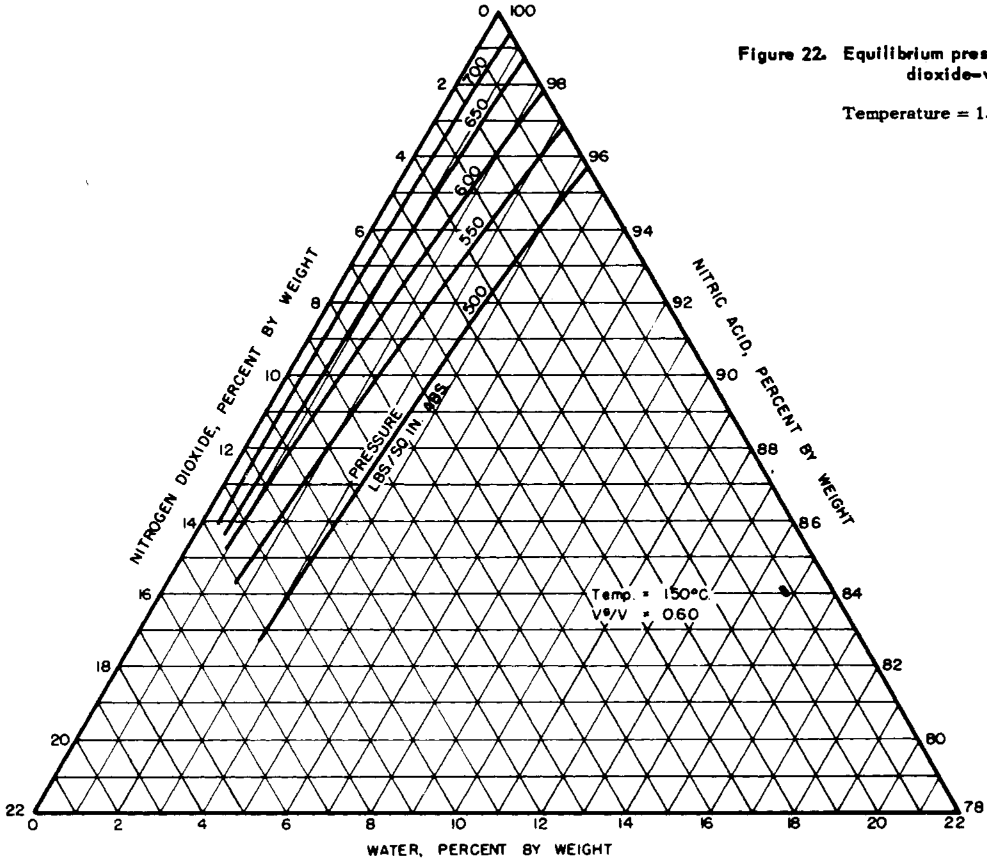


Figure 22. Equilibrium pressures in the nitric acid–nitrogen dioxide–water system

Temperature = 150°C., $V^G/V = 0.60$

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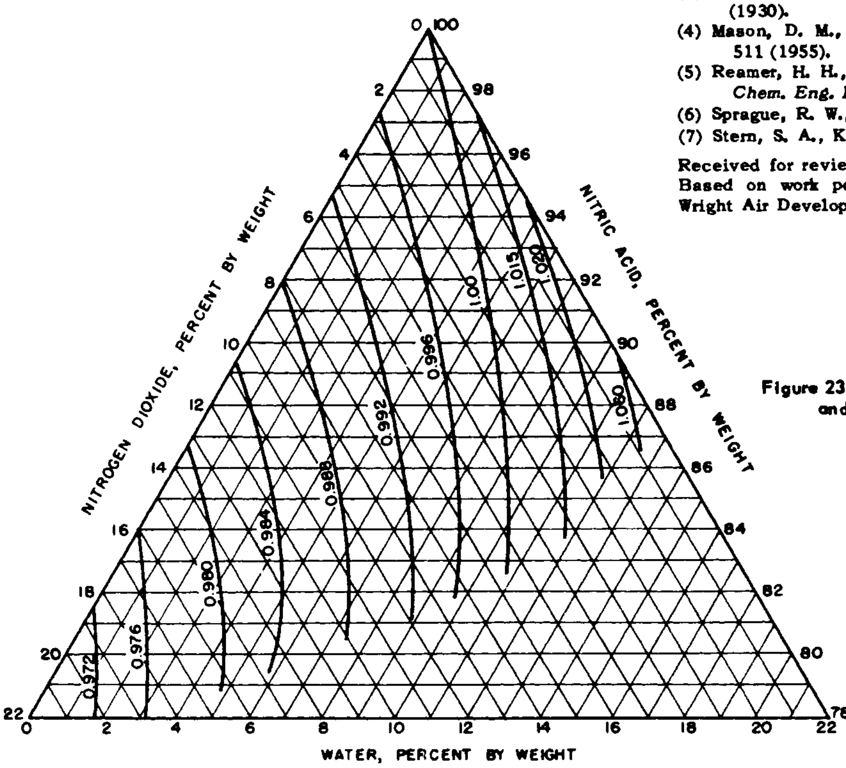

Figure 23. Generalized relation between specific volume and composition at constant temperature and constant V^G/V ratio