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Thermal Stability of Concentrated Nitric Acid

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Concentrated nitric acid containing more than 90 weight % of HNO_3, when confined in a closed container at room temperature and above, dissociates to form oxides of nitrogen, water, and oxygen. Because of the low solubility of the oxygen in the equilibrium mixture, considerable pressure may result if the ratio of the vapor volume to the liquid volume in the container is small. In view of the wide use of fuming nitric acid as a component of binary liquid rocket propellants and as a nitrating agent, a knowledge of the thermal stability, therefore, is of real practical importance in the handling and storage of the concentrated acid.

In the course of an investigation of the volumetric and phase behavior of concentrated nitric acid (*8-10*) *P-V-T* data were obtained at physicochemical equilibrium for mixtures of known initial composition. By the application of the principles of chemical thermodynamics to these data, information has been obtained on the chemical stability of the concentrated acid as a function of its initial composition.

ESTIMATION OF EQUILIBRIUM COMPOSITION

The dissociation of nitric acid in the heterogeneous vapor-liquid region is a kinetically complex reaction which is explained as proceeding according to the following steps (*6*):

$$\begin{aligned} 2\,HNO_3 &\rightleftarrows N_2O_5 + H_2O \\ N_2O_5 &\rightleftarrows N_2O_3 + O_2 \\ N_2O_3 &\rightleftarrows NO + NO_2 \\ NO + \tfrac{1}{2}O_2 &\rightleftarrows NO_2 \end{aligned}$$

The summation of these steps leads to the over-all stoichiometric relation

$$2\,HNO_3 = H_2O + N_2O_4 + \tfrac{1}{2}O_2 \qquad (1)$$

where N_2O_4 designates an equilibrium mixture of N_2O_4 and NO_2.

Because of the complexity of the solubility relations of oxygen and oxides of nitrogen and the paucity of data on the activity coefficients of the various species, calculation of the true thermodynamic equilibrium constants expressed in terms of the activities of the species is practically impossible. However, it is possible to calculate an apparent equilibrium "constant" in terms of the equilibrium mole fractions of nitric acid, nitrogen tetroxide, and water, defined as

$$K_x = \frac{(N_2O_4)\,(H_2O)}{(HNO_3)^2} \qquad (2)$$

For its calculation, the composition of the liquid phase at equilibrium conditions is needed. This was estimated on the basis of an oxygen material balance on the system and the stoichiometry of the dissociation reaction given by Equation 1. The oxygen balance on the system at equilibrium can be written (*9*) as

$$n_{O_2} = n^G_{O_2} + n^L_{O_2} \qquad (3)$$

$$= p_{O_2}\left[\frac{V^G}{z_{O_2}RT} + k_{O_2}V^L\right] \qquad (4)$$

where

n_{O_2} = total number of moles of oxygen in system at equilibrium formed from dissociation of nitric acid, at pressure p^∞ and temperature T
$n^G_{O_2}$ = number of moles of oxygen in gas phase
$n^L_{O_2}$ = number of moles of oxygen in liquid phase
p_{O_2} = partial pressure of oxygen in gas phase
V^G = volume of vapor phase at equilibrium
z_{O_2} = compressibility factor of oxygen at pressure p_{O_2} and temperature T
k_{O_2} = $C^L_{O_2}/p_{O_2}$ Henry's law constant for solubility of oxygen in liquid phase of equilibrium composition at temperature T
$C^L_{O_2}$ = concentration of oxygen in liquid phase
V^L = volume of liquid phase at equilibrium

The compressibility factor, z_{O_2}, obtained from a generalized compressibility chart, was found to be very nearly unity for the conditions investigated. The partial pressure of oxygen under equilibrium conditions, p_{O_2}, was obtained by correcting the total equilibrium pressure for the vapor pressures due to nitric acid, nitrogen dioxide, and water present in the liquid phase. For this purpose, the vapor pressure data for the ternary mixtures of nitric acid, nitrogen dioxide, and water, reported by McKeown and Belles (*11–13*) for 25°, 40°, and 60° C., were extrapolated to 85° C.

For a first approximation, the partial pressure of oxygen was assumed to be equal to the equilibrium pressure observed. By Equation 4, n_{O_2} was calculated and from the stoichiometry of the dissociation equation, the quantity of nitric acid dissociated and the quantities of nitrogen tetroxide and water formed, were obtained. From a knowledge of the initial composition, the equilibrium composition was then calculated. Its vapor pressure at 85° C. was estimated and subtracted from the observed equilibrium pressure to give a corrected value of the partial pressure of oxygen. The calculation was then repeated using this corrected p_{O_2}. After several trials the composition of the equilibrium liquid phase converged to a constant value.

In these calculations, Henry's law constant, k_{O_2}, was estimated from the work of Robertson, Mason, and Corcoran (*14*) and Kay and Stern (*9*), and an average value of 5.65×10^{-3} mole per liter-atmosphere at 85° C. was used.

RESULTS AND DISCUSSION

The equilibrium composition of each of the mixtures studied was calculated at 85° C. and the data were used in Equation 2 to calculate K_x. The results are summarized in Table I and are shown graphically in Figure 1, where the logarithm of the apparent equilibrium constant is plotted against the logarithm of the oxygen pressure at equilibrium. The relation is approximately a linear one for initially pure nitric acid and its binary and ternary mixtures with nitrogen dioxide and water over a range of oxygen pressures between 20 and 1200 p.s.i. and V^G/V ratios from 0.05 to 0.80.

The equation of this line is:

$$\log K_x = 0.25 \log p_{O_2} + C \qquad (5)$$

The product ($K_x \times p_{O_2}^{0.25}$), therefore, should be a constant. As will be seen in the table, this is approximately true. The deviations are due, probably, to uncertainties in the estimation of the partial pressure of oxygen and in the equilibrium composition as well as in the calculation of K_x. It is estimated that the calculated partial pressures and equilibrium compositions are accurate to within ±3%. The fact that the deviations are greatest in the high pressure region would seem to indicate that better agreement might be expected if the activities of the species instead of their mole fractions were used to calculate K_x.

Because the partial pressure of oxygen exerts an effect only as the fourth root, it is evident that the effect of oxygen on the equilibrium is very small compared to the effect of nitrogen tetroxide and water. Consequently, the dissociation can be suppressed much more effectively by

Table I. Correlation of Equilibrium Data

Temperature, 85 °C.

Initial Composition, Weight %			Sp. Vol., Cu.Ft./Lb.	V^G/V	Equil. Press., P.S.I.A.	Partial Press. O_2, P.S.I.A.	Equilibrium Composition, 6 Wt., %			$K_x \times 10^3$	1/4 $K_x p_{O_2}$
HNO_3	NO_2	H_2O					HNO_3	NO_2	H_2O		
100.00	0.00	0.00	0.01278	0.138	1183	1147	86.64	11.18	2.19	7.81	45.4
....	....	....	0.01393	0.208	902	866	86.72	11.11	2.18	7.70	42.2
....	....	....	0.01640	0.330	618	582	86.32	11.43	2.24	8.22	40.4
....	....	....	0.01932	0.433	465	429	85.82	11.87	2.32	8.97	40.8
92.50	7.50	0.00	0.01244	0.113	878	823	83.79	14.80	1.41	7.09	38.0
....	....	....	0.01381	0.211	632	578	83.58	14.98	1.44	7.40	36.3
....	....	....	0.01861	0.421	359	304	82.97	15.49	1.55	8.33	34.8
....	....	....	0.04416	0.765	152	97	81.25	16.93	1.82	11.21	35.2
85.00	15.00	0.00	0.01208	0.100	640	575	79.31	19.78	0.91	6.86	33.5
....	....	....	0.01340	0.191	479	414	79.05	20.00	0.95	7.27	32.7
....	....	....	0.01848	0.421	270	206	78.56	20.41	1.03	8.19	30.9
....	....	....	0.04562	0.772	133	68	76.70	21.97	1.33	11.86	33.9
70.00	30.00	0.00	0.01363	0.217	229	134	67.90	31.77	0.33	....	....
97.50	0.00	2.50	0.01277	0.116	739	709	89.84	6.39	3.77	7.16	37.0
....	....	....	0.01426	0.216	516	486	89.74	6.46	3.80	7.30	34.3
....	....	....	0.01759	0.374	328	298	89.40	6.74	3.86	7.79	32.4
....	....	....	0.03689	0.708	138	108	87.74	8.13	4.13	10.45	33.7
95.00	0.00	5.00	0.01190	0.048	595	570	90.92	3.57	5.51	7.35	36.0
....	....	....	0.01252	0.086	493	468	90.55	3.68	5.77	6.20	29.0
....	....	....	0.01406	0.188	348	323	90.36	3.84	5.81	6.53	27.6
....	....	....	0.01961	0.429	202	177	89.12	4.87	6.01	8.50	30.9
....	....	....	0.05633	0.814	76	51	87.19	6.49	6.31	12.91	34.5
90.00	0.00	10.00	0.01363	0.149	147	135	88.27	1.42	10.31	....	....
94.70	4.69	0.61	0.01363	0.187	654	609	85.95	12.02	2.04	7.95	39.8
84.56	13.66	1.78	0.01363	0.190	178	118	82.87	15.08	2.06	10.81	35.6
79.22	18.37	2.41	0.01363	0.195	82	17	78.98	18.57	2.45	17.49	35.2
72.37	24.44	3.19	0.01363	0.196	80	1.00	72.37	24.44	3.19	....	....
....	....	....	0.02371	0.561	79	0.50	72.39	24.42	3.19	....	....
86.05	11.71	2.24	0.01363	0.185	176	126	84.27	13.20	2.53	11.27	37.8
81.29	15.65	3.06	0.01363	0.186	78	23	80.96	15.92	3.12	18.15	39.8
76.61	19.56	3.83	0.01363	0.205	72	7	76.51	19.64	3.85	....	....
95.00	3.59	1.41	0.01363	0.182	580	540	87.47	9.90	2.63	8.15	39.2
....	....	....	0.01762	0.375	340	300	86.80	10.45	2.75	9.14	38.0
....	....	....	0.02389	0.538	232	192	85.95	11.15	2.90	10.49	39.0
90.00	7.18	2.82	0.01363	0.194	222	182	87.38	9.36	3.26	9.57	35.2
....	....	....	0.02371	0.535	134	94	86.04	10.31	3.65	12.18	38.4
85.00	10.77	4.23	0.01363	0.176	80	35	84.65	11.09	4.26	15.81	38.4
....	....	....	0.02371	0.533	70	25	83.83	11.76	4.42	17.71	39.6
80.00	14.36	5.64	0.01363	0.178	58	3	79.98	14.38	5.64	....	....

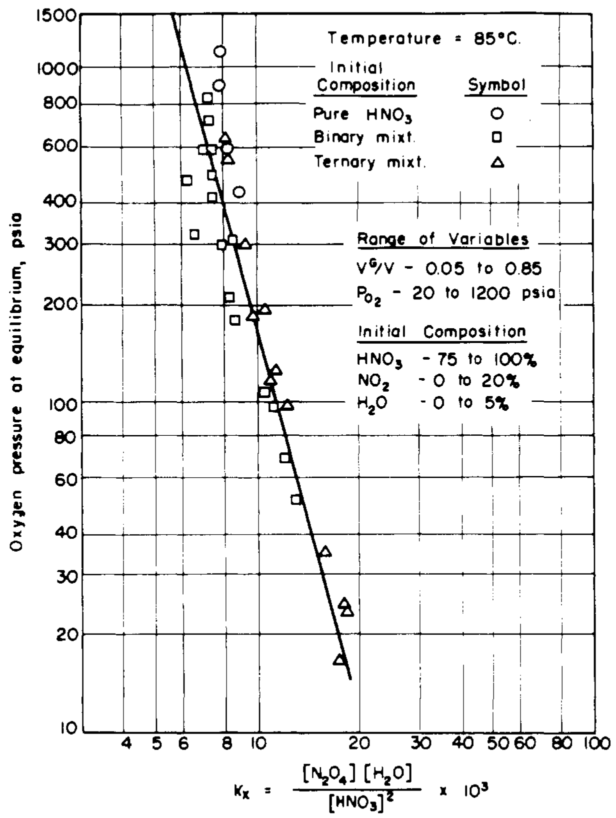

Figure 1. Relation between oxygen pressure at equilibrium and apparent equilibrium constant calculated in terms of final mole fractions with nitrogen dioxide expressed as N_2O_4

nitrogen tetroxide and water as additives than by oxygen. Conversely, it may be expected that the equilibrium will be disturbed very little by the removal of oxygen from the system as the reaction proceeds, but will be affected considerably by the removal of nitrogen tetroxide and water. The relative effects of nitrogen tetroxide and water are satisfactorily explained on the basis of molecular species N_2O_4 and H_2O. Hence, on a weight basis, water is expected to be about five times as effective as nitrogen tetroxide.

The calculated compositions of the liquid phase at physicochemical equilibrium at 85° C. are plotted on the triangular diagram (Figure 2). None of the equilibrium mixtures contain more than about 91% of nitric acid, indicating that acids of this strength and above are unstable and would decompose spontaneously at this temperature. On the other hand, ternary mixtures containing 80% of nitric acid and more than 6% of water are stable. Compositions between these two extremes are stable only under oxygen pressure (50 to 1500 p.s.i.a.).

The effect of temperature on the degree of dissociation of pure nitric acid at physicochemical equilibrium was calculated in the range from 76° to 125° C. by Kay and Stern (*9*). In those calculations, the partial pressure of oxygen, p_{O_2}, was assumed as being equal to the total pressure because of a lack of data on vapor pressures in the ternary system nitric acid-nitrogen dioxide-water. These values have now been corrected for the partial pressures of nitric acid, nitrogen dioxide, and water in the vapor phase and the results, including the new values of the Henry's law constant, are summarized in Table II. Also listed are the corresponding compositions of the liquid phase both as weight per cent of nitric acid, nitrogen dioxide, and water and as weight per cent of nitric acid and weight per cent of nitrous acid. The latter are based on the equilibrium

$$HNO_3 \rightleftarrows HNO_2 + 1/2\ O_2 \qquad (6)$$

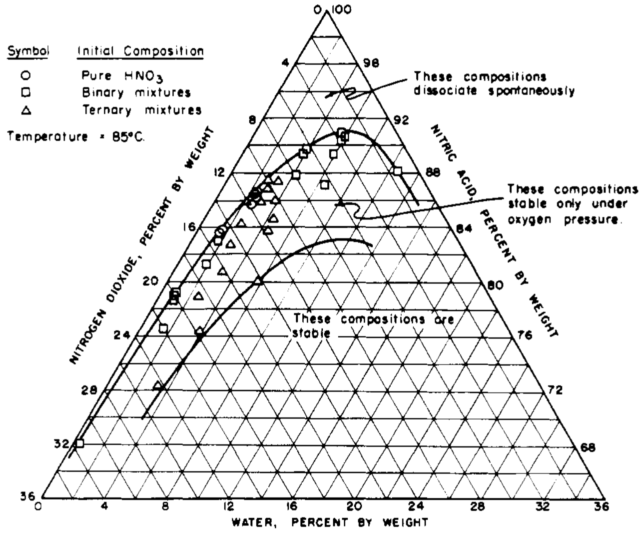

Figure 2. Liquid phase compositions at equilibrium for various initial compositions in the nitric acid–nitrogen dioxide-water system at 85° C.

Table II. Calculated Values of Degree of Dissociation of Pure Nitric Acid, Henry's Law Constant for Oxygen in Nitric Acid, and Liquid Phase Compositions at Physicochemical Equilibrium

			Equilibrium Composition Weight %				
		k_{O_2} Corr., Mole/Liter-Atm.	Equation 1			Equation 6	
Temp., °C.	α Corr.	×10³	HNO_3	N_2O_4	H_2O	HNO_3	HNO_2
76	0.139	5.18	87.64	10.33	2.02	94.72	5.28
85	0.148	5.54	86.63	11.02	2.16	94.37	5.63
95	0.158	5.95	85.93	11.78	2.31	93.98	6.02
105	0.168	6.39	85.00	12.54	2.45	93.60	6.40
115	0.179	6.86	84.01	13.37	2.62	93.17	6.83
125	0.191	7.40	82.91	14.29	2.80	92.70	7.30

α = degree of dissociation of nitric acid.

It is seen that the degree of dissociation increases with temperature.

These calculations are of interest not only in the handling and storage of nitric acid but also in the manufacture of concentrated nitric acid from liquid nitrogen dioxide, water, and oxygen under pressure (*3*, *4*), wherein the same equilibrium is approached from the other side.

$$N_2O_4 + H_2O + 1/2\ O_2 \rightleftarrows 2HNO_3 \qquad (7)$$

The maximum concentration attainable in this process for various conditions can be estimated for 85° C. from results shown in Figure 1 and Table I. Similar calculations for other temperatures may be made using the data presented earlier (*8*). The earlier work of Gaddy (*7*) shows, erroneously, an increase in equilibrium concentration of nitric acid with temperature when a mixture of nitrogen dioxide, water, and oxygen in stoichiometric proportions is agitated in an autoclave. The time to reach equilibrium was stated to be 0.5 hour. The results reported by the authors as well as that of Fauser (*3*) indicate a much longer time for the attainment of equilibrium. Ellis and Murray (*2*), on the basis of thermodynamic data of Forsythe and Giauque (*5*), showed that the equilibrium degree of dissociation of nitric acid in the vapor phase increases with temperature.

NOMENCLATURE

c = concentration
n = number of moles
p = pressure
R = universal gas constant
T = temperature, absolute
V = volume
Z = compressibility factor

Superscripts

G = vapor phase
L = liquid phase
∞ = at physicochemical equilibrium

Subscript

O_2 = for oxygen

Composite symbols

k_{O_2} = Henry's law constant for oxygen
K_x^2 = apparent equilibrium constant in terms of mole fractions

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Single Generalized Chart of Detonation Parameters for Gaseous Mixtures

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There exists a need for simplified methods of determining and visualizing the values of detonation parameters for all gaseous mixtures. Some of the instability phenomena observed in aircraft propulsion systems (turbojet afterburner, ramjet, rocket) are believed to be the result of some form of detonation. Information on detonation parameters may have direct application in the understanding of these instabilities. These instability phenomena and their possible association with detonative combustion have been discussed (*1, 5, 6*).

Information relating to aircraft propulsion system instability phenomena can be applied to analogous situations in chemical and other industries. Thus, fundamental aspects of detonation are likely to find application in many areas.

To provide simplified means for analytically determining values of detonation parameters, the authors rearranged the classical equations of detonation and devised a calculation procedure based on the resulting generalized equations, involving only nondimensional quantities (*2*). During the process of generalizing the detonation equations, it became apparent that it would be extremely useful if the detonation parameters for all gaseous mixtures could be presented in nondimensional form on a Mollier-type diagram. This would aid considerably in the visualization of the relationships among the various detonation parameters. It was found that the generalized detonation equations could be utilized for the graphical presentation of detonation parameters on a small number of Mollier-type diagrams. Three such diagrams were presented (*7*), covering the ranges of detonation parameters normally encountered for gaseous mixtures.

In this report, a single generalized chart of detonation parameters for gaseous mixtures is presented. This chart represents an improvement of the generalized charts previously presented (*7*), in that the detonation parameters for all gaseous mixtures are now on a single diagram rather than on a series of diagrams, thereby eliminating the necessity for interpolation between charts. The chief usefulness of the generalized chart is to provide a means for the visualization of the relationships among the detonation parameters for all gaseous mixtures on a single diagram. The application of the single generalized chart is illustrated by several examples.

EQUATIONS FOR GENERALIZED CHART

It has been shown (*2*) that the following four equations can be derived directly from the classical equations describing the detonation process for gaseous mixtures:

$$B = \frac{1}{\gamma_2^2 - 1}\left[\frac{M_1^2}{2} + \left(\frac{\gamma_2}{\gamma_1}\right)^2\left(\frac{1}{2M_1^2} + \gamma_1\right)\right] - \frac{1}{\gamma_1 - 1} \qquad (1)$$

$$\frac{p_2}{p_1} = \frac{1}{\gamma_2 + 1}\,(\gamma_1 M_1^2 + 1) \qquad (2)$$

$$\frac{\rho_2}{\rho_1} = \frac{\gamma_2 + 1}{\gamma_2}\left(\frac{\gamma_1 M_1^2}{\gamma_1 M_1^2 + 1}\right) \qquad (3)$$

$$\frac{T_2 M_{w_1}}{T_1 M_{w_2}} = \frac{\gamma_2}{(\gamma_2 + 1)^2}\cdot\frac{(\gamma_1 M_1^2 + 1)^2}{\gamma_1 M_1^2} \qquad (4)$$

where B is the energy release function, $B = (Jh/a_1^2)$, and M_1 is the detonative Mach number, $M_1 = (D/a_1)$.

In the derivation of these equations it was assumed that the ideal gas law holds for the reactants and the products at the initial and final conditions, respectively. This is equivalent to the assumption that the actual temperatures and pressures of the initial and final mixtures in all cases are in a region where the use of the ideal gas law results in negligible error. For the final mixture, this is a reasonable assumption in all cases in view of the extremely high temperatures occurring in detonation. For the initial mixture, this is a reasonable assumption if the initial conditions are sufficiently far from the critical conditions of pressure and temperature for each component so that compressibility is a negligible factor. Thus, in all cases where an equation of state has been required for describing the states of the initial and final mixtures at the initial and final conditions, respectively, the ideal gas law has been used. The usual assumption is also made that chemical equilibrium is attained in the detonation wave.