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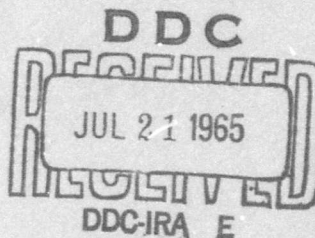
MAY 1965

Prepared by E. T. CHANG, N. A. GOKCEN, and C. D. ROBISON
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ABSTRACT

The solubilities of O_2, NO, and N_2O_3 in liquid N_2O_4 have been measured over a wide pressure range at -11.03, 0.0, and 25°C. The results show, conclusively, that Henry's law is obeyed for all pressures at each temperature for O_2 and at low pressures for NO and N_2O_3. The standard free energy, enthalpy, and entropy of solution for each gas have been computed.

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FIGURES

TABLES

I. INTRODUCTION

The solubilities of a number of gases in propellants and oxidizers have been measured during the past two years (Refs. 1, 2). This report, a continuation of the foregoing effort, presents the experimental results and their interpretation for O_2, NO, and N_2O_3 in liquid N_2O_4 at various pressures and at -11.03, 0.0, and 25.0°C.

A literature search revealed that there were no data on the solubility of O_2 in liquid N_2O_4. Numerous investigations on systems containing NO, N_2O_4, NO_2, and N_2O_3 were reported, but the results were inconclusive and gave no direct solubility data for NO in liquid N_2O_4. A systematic and reliable investigation of O_2, NO, and N_2O_3 in liquid N_2O_4 was therefore warranted.

II. EXPERIMENTAL PROCEDURE

The apparatus and procedure for the solubility measurements are described in Ref. 2. In this work research grade N_2O_4 of 99.5 percent minimum purity was further purified as follows: Oxygen was bubbled through N_2O_4 to oxidize NO and NOCl. Then, liquid N_2O_4 was repeatedly degassed, frozen with liquid N_2, evacuated, and melted, and this procedure was repeat. until N_2O_4 froze to a white solid. The solid was then melted and distilled under a vacuum into a sample container. Samples of approximately 100 g of liquid N_2O_4 were used for the solubility measurements on O_2 and samples of approximately 5 g for the measurements on NO. The gaseous O_2 for the solubility measurements was of 99.99 percent minimum purity. The research grade NO gas had the following analysis in weight percent: 0.68 N_2, 0.33 N_2O, 0.22 NO_2, and 98.74 NO. The gas was passed through a tube containing ascarite to remove NO_2 before being used in the experiments.

III. RESULTS AND DISCUSSION

It is shown in the earlier reports (Refs. 1, 2) that the gases dissolved in liquids of interest obeyed Henry's law, i.e., the solubility is proportional to the partial pressure of dissolved gas. Thus, the process of dissolving a nonreacting gas in N_2O_4 can be considered as the simple reaction

$$\text{gas} \longrightarrow \text{dissolved gas} \tag{1}$$

with its equilibrium constant K defined by

$$K = \frac{\text{mol fraction of dissolved gas}}{\text{partial pressure of gas}} = \frac{X}{P} \tag{2}$$

The data presented in this report show that Eq. (2) is valid for O_2 at all pressures and for NO and N_2O_3 at low pressures. When NO is admitted in the apparatus for the measurements of solubility, it reacts with gaseous NO_2 (or N_2O_4) to form N_2O_3, and large solubilities of NO and N_2O_3 in liquid N_2O_4 affect the concentrations of gaseous NO_2 and N_2O_4. It is therefore necessary to account for the simultaneous reactions $NO(g) + NO_2(g) = N_2O_3(g)$ and $N_2O_4(g) = 2NO_2(g)$ in computing the partial pressures of each gas over the liquid and finding the composition of the solution.

A. OXYGEN

The solubility values for O_2 are listed in Table 1 and are represented in Fig. 1. Aside from a small degree of scattering, which is less than $\pm 0.05 \times 10^{-4}$ in K (shown by $\pm$ in Fig. 1), the temperature dependence of the equilibrium constant for solubility is linear. The equation representing this relationship is

Table 1. Solubility of O_2 in Liquid N_2O_4

| Run No.	T, °K	P, atm	X(mol fr)x 10^3	K = X/P x 10^3
0 - 1	298.15	0.3728	0.376	1.01
0 - 2	298.15	0.4989	0.516	1.03
0 - 3	298.15	0.5745	0.597	1.04
0 - 4	298.15	0.9963	1.008	1.01
0 - 5	298.15	1.0809	1.070	<u>0.99</u>
			Average	1.02
0 - 6	273.15	0.2643	0.243	0.92
0 - 7	273.15	0.6275	0.578	0.92
0 - 8	273.15	1.1241	1.030	0.92
0 - 9	273.15	1.7950	1.637	<u>0.91</u>
			Average	0.92
0 - 10	262.02	0.6041	0.534	0.88
0 - 11	262.02	1.2017	1.058	0.88
0 - 12	262.02	1.3091	1.147	0.88
0 - 13	262.02	1.6119	1.423	0.88
0 - 14	262.02	1.9876	1.740	<u>0.88</u>
			Average	0.88
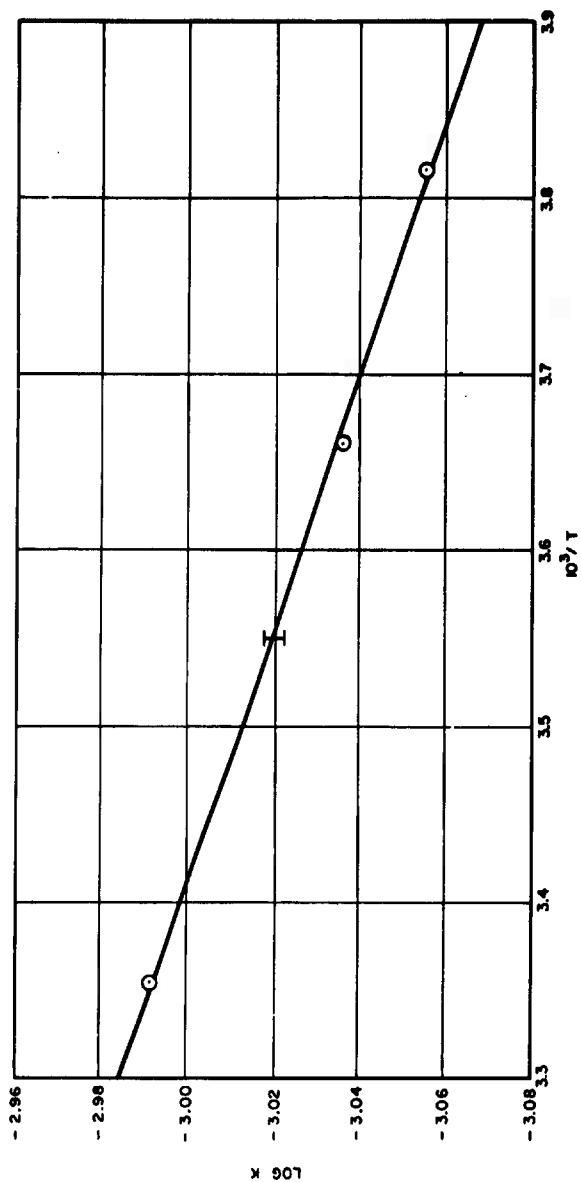
Fig. 1. Solubility of O_2 in Liquid N_2O_4

$$\log K = -\frac{139}{T} - 2.526 \qquad (3)$$

The corresponding change in the standard free energy ΔG° is

$$\Delta G^{\circ} = 636 + 11.56 \text{ T} \qquad (4)$$

where $\Delta H^{\circ} = 636$ cal/mole and $\Delta S^{\circ} = -11.56$ cal/mole $^{\circ}$K.

A possible reaction of oxygen with N_2O_4 is

$$O_2(g) + 2N_2O_4(l) \rightleftharpoons 2N_2O_5 \text{ (in liquid } N_2O_4) \qquad (5)$$
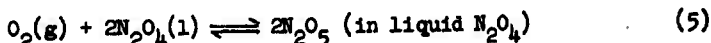
For this reaction the equilibrium constant is $(2X)^2/p_{O_2}$, where $2X$ is the mol fraction of N_2O_5. The dissolution process for O_2 in liquid N_2O_4 is represented by (1) and not by (5) because X/p_{O_2} is a constant and not $(2X)^2/p_{O_2}$ at various pressures for a given temperature.

B. NITRIC OXIDE AND DINITROGEN TRIOXIDE

In order to determine the partial pressures of the various species over liquid N_2O_4 from the measurement of total pressure it is necessary to consider the two side reactions. Gaseous N_2O_4 dissociates reversibly into two molecules of NO_2 in the gas phase, i.e.,

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad (6)$$

In the liquid state N_2O_4 dissociates so little that it may safely be considered as entirely N_2O_4 (Ref. 3). In addition NO reacts with NO_2 to form N_2O_3 as follows:

$$NO(g) + NO_2(g) \rightleftharpoons N_2O_3(g) \qquad (7)$$
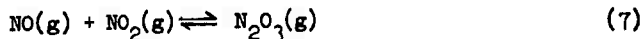
At equilibrium in this system, the molecular species NO, NO_2, N_2O_4, and N_2O_3 are present. The amount of each species present in the gas phase is determined by the following equilibrium constants for (6) and (7):

$$K_{N_2O_4} = \frac{P_{NO_2}^2}{P_{N_2O_4}} \qquad (8)$$

$$K_{N_2O_3} = \frac{P_{NO}P_{NO_2}}{P_{N_2O_3}} \qquad (9)$$

The evaluation of partial pressure of NO and mol fraction of NO dissolved is not straightforward. However, an analytical expression can be obtained in the following manner: Reaction (6) can be written as the difference of the reactions

$$N_2O_4(1) \Longleftrightarrow 2NO_2(g) \qquad (10)$$

$$N_2O_4(1) \Longleftrightarrow N_2O_4(g) \qquad (11)$$

Their respective equilibrium constants are

$$K_1 = \frac{P_{NO_2}^2}{X_{N_2O_4}} \qquad (12)$$

$$K_2 = \frac{P_{N_2O_4}}{X_{N_2O_4}} \qquad (13)$$

where $X_{N_2O_4}$ is the mole fraction of N_2O_4 in the liquid phase.

The experimentally measured total pressure over the liquid phase of this system is the sum of the partial pressures:

$$P_{total} = P_{N_2O_4} + P_{NO_2} + P_{NO} + P_{N_2O_3} \tag{14}$$

From (12), (13), (9), and (14) the partial pressures are, respectively,

$$P_{NO_2} = \left(K_1 X_{N_2O_4}\right)^{1/2} \tag{15}$$

$$P_{N_2O_4} = K_2 X_{N_2O_4} \tag{16}$$

$$P_{N_2O_3} = \frac{P_{NO}P_{NO_2}}{K_{N_2O_3}} = \frac{P_{NO}\left(K_1 X_{N_2O_4}\right)^{1/2}}{K_{N_2O_3}} \tag{17}$$

$$P_{NO} = \frac{P_{total} - K_2 X_{N_2O_4} - \left(K_1 X_{N_2O_4}\right)^{1/2}}{1 + \left[\left(K_1 X_{N_2O_4}\right)^{1/2} \big/ K_{N_2O_3}\right]} \tag{18}$$

The equilibrium constants can be calculated from thermodynamic data in the JANAF Tables (Ref. 4). The calculated values used are listed in Table 2.

Table 2. Values of Equilibrium Constants

T, $^{\circ}$C	K_1	K_2	$K_{N_2O_3}$
25.0	0.1238	0.8454	2.358
0	4.914×10^{-3}	0.2765	0.5437
-11.03	9.629×10^{-4}	0.1556	0.2604

Finally, by the method of successive approximation, the partial pressures
and the mol fractions of the solute gas are evaluated. For the first approx-
imation, the mol fraction of N_2O_4, $X_{N_2O_4}$, is set to unity in Eqs. (15)-(18) to
obtain the partial pressures of all four species. These values and the
known volume above the liquid yield the mass of each constituent, the mol
fraction $X_{N_2O_4}$ of liquid N_2O_4. Substitution of $X_{N_2O_4}$ in Eqs. (15)-(18) yields
a second set of values for the partial pressures from which $X_{N_2O_4}$ is recal-
culated. The procedure may be repeated to obtain the third approximation
for $X_{N_2O_4}$ which differs from the second approximation by less than 0.1
percent.

The solubility values for NO in liquid N_2O_4 are listed in Table 3 and
are represented in Figs. 2-4.

Figure 2 presents the solubility, as mol fraction X_{NO}, of NO in liquid
N_2O_4 vs the partial pressure of NO. It is assumed that only the species NO
and N_2O_4 are present in the liquid phase. The plot shows that only in the
dilute solution region, i.e., when $X_{NO} < 0.1$, Henry's law is obeyed. The
solubility of NO in liquid N_2O_4 decreases as temperature increases. Log $X_{NO}/P_{NO} =$
log K′ is presented vs $X^2_{N_2O_4}$ in Fig. 3 to facilitate the extrapolation
of the solubility constant K′, to the limiting value of zero concentra-
tion of NO. The decrease in K′ with increase in pressure is probably due
to the deviation of the gases from the ideal gas laws. Figure 4 represents
log K′ vs 1/T with mol fraction X_{NO} as a parameter. The curves appear linear
up to the concentration of $X_{NO} = 0.2$. The equation representing the linear
plots of Fig. 4 and the curves in the linear portions of Fig. 3 is

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Table 3. Solubility of NO in Liquid N_2O_4

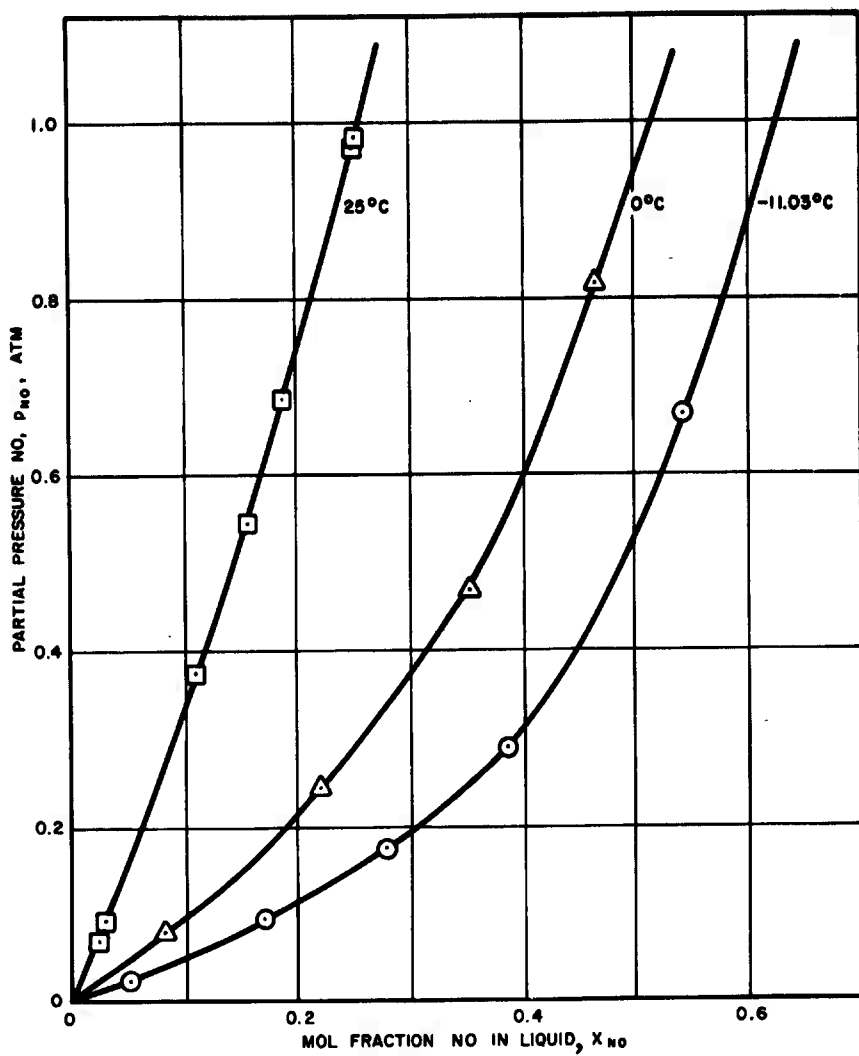| Run No.	$T, {}^\circ K$	P_{total}, atm	X_{NO}	$X_{N_2O_4}$	$(X_{N_2O_4})^2$	P_{NO}, atm	K'	Log K'
NO- 1	262.12	0.2041	0.0514	0.9486	0.8998	0.0236	2.1780	0.3381
NO- 2	262.12	0.2597	0.1705	0.8295	0.6881	0.0924	1.8452	0.2660
NO- 3	262.12	0.3282	0.2799	0.7201	0.5185	0.1724	1.6235	0.2104
NO- 4	262.12	0.4343	0.3830	0.6170	0.3807	0.2870	1.3346	0.1254
NO- 5	262.12	0.8120	0.5424	0.4576	0.2094	0.6661	0.8143	-0.0892
			0.625[a]			1.000		
NO- 6	273.15	0.4097	0.0807	0.9193	0.8451	0.0786	1.0267	0.0114
NO- 7	273.15	0.5488	0.2211	0.7789	0.6067	0.2438	0.9069	-0.0426
NO- 8	273.15	0.7530	0.3513	0.6487	0.4208	0.4684	0.7500	-0.1249
NO- 9	273.15	1.0913	0.4653	0.5347	0.2859	0.8152	0.5708	-0.2435
			0.516[a]			1.000		
NO-10	298.15	1.2507	0.0234	0.9766	0.9537	0.0674	0.3472	-0.4597
NO-11	298.15	1.6583	0.1551	0.8449	0.7139	0.5456	0.2842	-0.5464
NO-12	298.15	2.0412	0.2541	0.7459	0.5564	0.9805	0.2592	-0.5864
NO-13	298.15	1.2721	0.0305	0.9695	0.9399	0.0926	0.3293	-0.4824
NO-14	298.15	1.5124	0.1097	0.8903	0.7926	0.3748	0.2927	-0.5340
NO-15	298.15	1.7799	0.1877	0.8123	0.6598	0.6840	0.2744	-0.5616
NO-16	298.15	2.0346	0.2501	0.7499	0.5624	0.9704	0.2577	-0.5889
			0.257[a]			1.000		

[a] The value of X_{NO} at $P_{NO} = 1$.

Fig. 2. Solubility of NO in Liquid N_2O_4

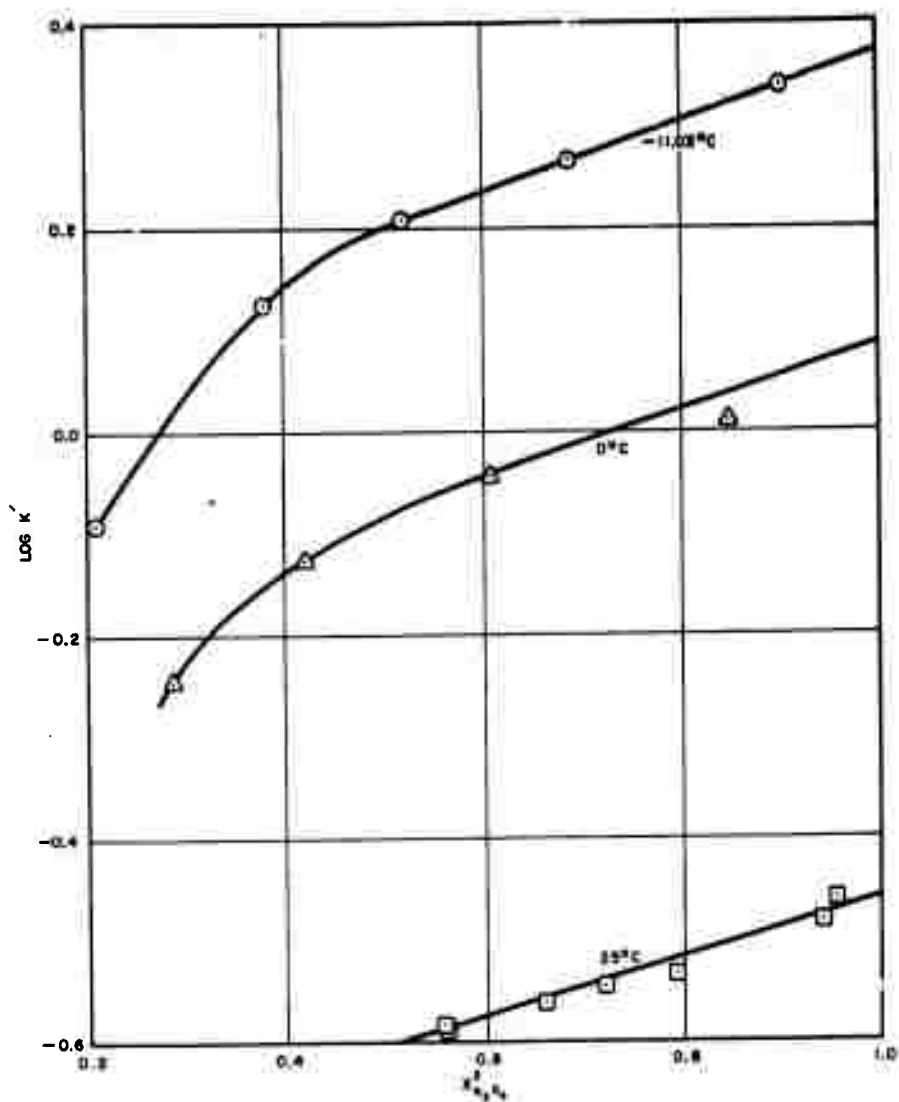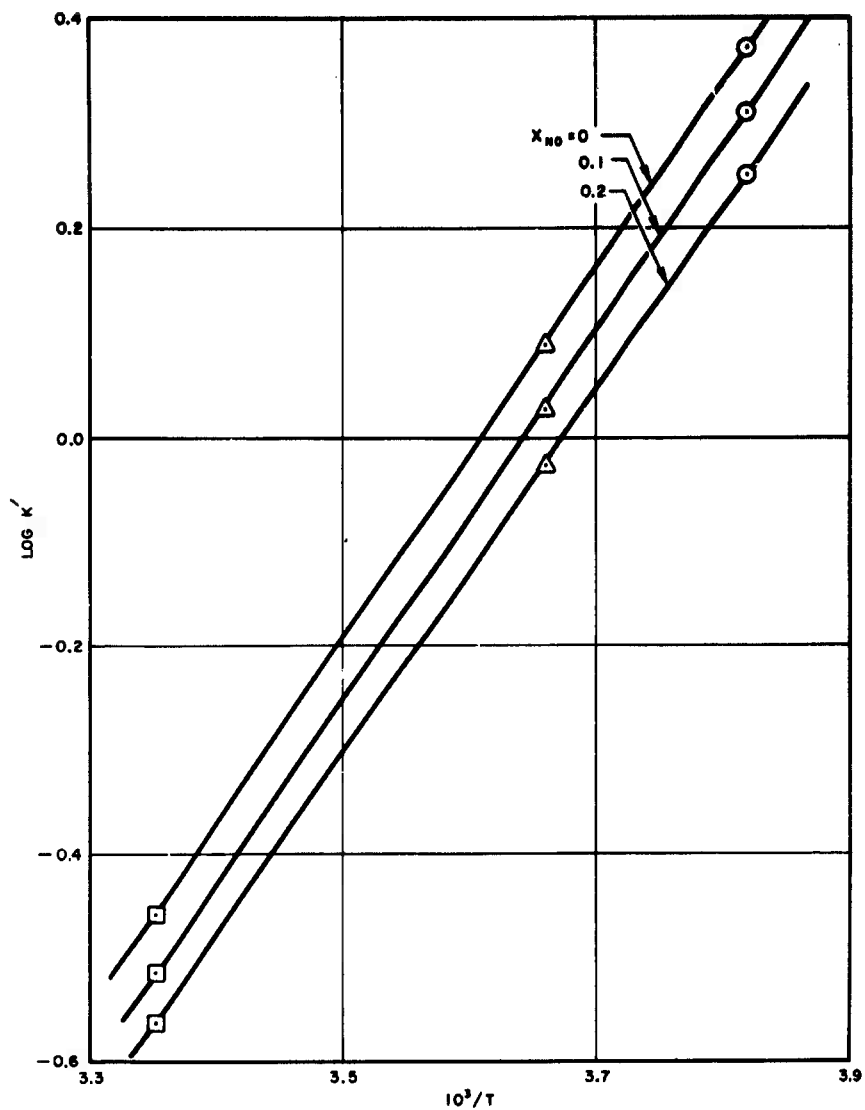Fig. 3.   Variation of Log K' with $X^2_{N_2O_4}$ in Liquid

Fig. 4. Variation of Log K' with Temperature at Fixed Compositions

T, °C	$x_{N_2O_4}$	x_{NO}	γ_1	$P_{N_2O_4}$	$x^g_{N_2O_4}$	P_{NO_2}	$x^g_{NO_2}$	P_{NO}	x^g_{NO}	$P_{N_2O_3}$	$x^g_{N_2O_3}$	γ_g	P_{total}
-11.03	0.949	0.051	1.974	0.1476	0.723	0.0302	0.148	0.0256	0.116	0.0027	0.013	1.985	0.2041
	0.829	0.171	1.907	0.1290	0.497	0.0283	0.109	0.0934	0.356	0.0100	0.039	1.743	0.2597
	0.720	0.280	1.837	0.1121	0.342	0.0363	0.080	0.1724	0.525	0.0178	0.053	1.595	0.3382
	0.617	0.383	1.763	0.0960	0.221	0.0244	0.056	0.2870	0.661	0.0269	0.062	1.457	0.4343
	0.458	0.542	1.688	0.0712	0.088	0.0210	0.025	0.4661	0.820	0.0357	0.066	1.332	0.6140
0.0	0.919	0.081	1.958	0.2542	0.620	0.0672	0.164	0.0785	0.192	0.0097	0.024	1.869	0.4097
	0.779	0.221	1.876	0.2254	0.392	0.0619	0.113	0.2458	0.444	0.0277	0.051	1.697	0.5488
	0.649	0.351	1.787	0.1794	0.238	0.0565	0.075	0.4654	0.622	0.0487	0.065	1.513	0.7530
	0.535	0.465	1.697	0.1478	0.135	0.0513	0.047	0.8352	0.747	0.0770	0.071	1.332	1.0913
25.0	0.977	0.023	1.988	0.8856	0.660	0.3477	0.278	0.0674	0.054	0.0099	0.008	1.973	1.3507
	0.970	0.030	1.995	0.8196	0.644	0.3463	0.272	0.0985	0.073	0.0136	0.011	1.990	1.2772
	0.890	0.110	1.942	0.7528	0.498	0.3380	0.220	0.3748	0.248	0.0528	0.035	1.816	1.5124
	0.845	0.155	1.916	0.7144	0.431	0.3334	0.195	0.5466	0.339	0.0748	0.045	1.747	1.6683
	0.812	0.188	1.896	0.6668	0.386	0.3171	0.178	0.6580	0.364	0.0920	0.052	1.697	1.7799
	0.750	0.250	1.857	0.6341	0.312	0.3047	0.150	0.9704	0.477	0.1234	0.062	1.668	2.0346
	0.746	0.254	1.854	0.6306	0.379	0.3038	0.149	0.9805	0.480	0.1263	0.062	1.604	2.0412

Table 4. Equilibrium Compositions of Liquid and Gas Phases for Mixtures of N_2O_4 and NO

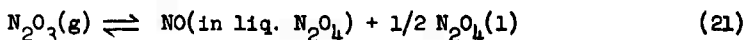$$\log K' = \log \frac{X_{NO}}{P_{NO}} = \frac{1682.6 + 87.4 X_{N_2O_4}^2}{T} - 6.388 \qquad (19)$$

The corresponding change in the standard free energy for the limiting case when $X_{N_2O_4} \longrightarrow 1$ is

$$\Delta G^O = -RT \ln K' = -8100 + 29.23 \, T \qquad (20)$$

where $\Delta H^O = -8100$ cal/mol, and $\Delta S^O = -29.23$ cal/mol^{O}K.

The values for the equilibrium composition of the liquid and gas phases and equilibrium partial pressures at -11.03, 0, and 25°C and at various total pressures are listed in Table 4. Figure 5 presents the equilibrium partial pressures of the molecular species NO, N_2O_3, N_2O_4, and NO_2 over the liquid. Since there are no data on the liquid phase equilibria, $NO(1) + NO_2(1) \rightleftharpoons N_2O_3(1)$ and $NO(1) + 1/2 \, N_2O_4(1) \rightleftharpoons N_2O_3(1)$, the liquid phase compositions are computed on the basis that only NO and N_2O_4 exist in the liquid. The compositions are also expressed as a function of y_1 and y_g, the total oxygen to total nitrogen ratio in the formula NO_y of the liquid and of the gas phase, respectively.

The partial pressure of N_2O_3 over the liquid N_2O_4 containing dissolved species from the gas phase have been computed and listed in Table 4. A possible reaction for the dissolution process of gaseous N_2O_3 in liquid N_2O_4 may be assumed as follows:

$$N_2O_3(g) \rightleftharpoons NO(in \; liq. \; N_2O_4) + 1/2 \, N_2O_4(1) \qquad (21)$$

Then, the solubility constant $K'' = X_{NO}/P_{N_2O_3}$ of gaseous N_2O_3 in liquid N_2O_4 may be represented by
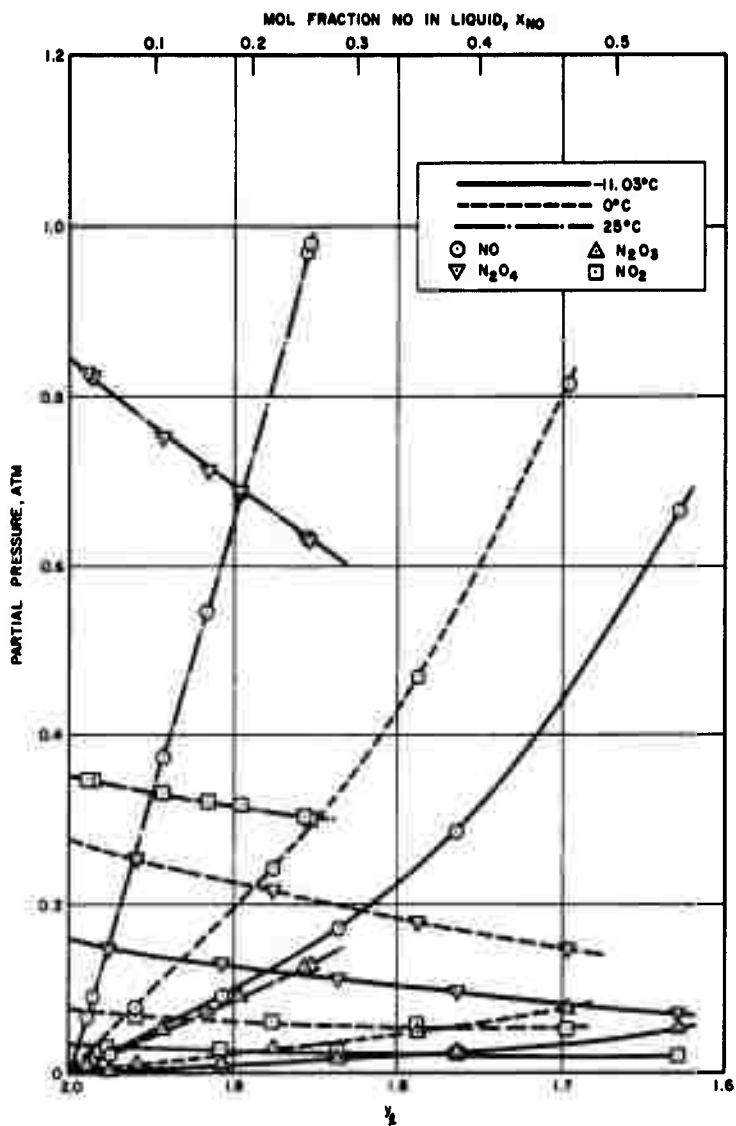
Fig. 5. Partial Pressures of NO, N_2O_3, N_2O_4, and NO_2 vs
Atomic Ratio $O/N = y_1$ in Liquid

$$\log K'' = \log \frac{X_{NO}}{P_{N_2O_3}} = \frac{199.2}{T} - 6.33 \tag{22}$$

for the limiting case when $X_{NO} \longrightarrow 0$. This equation is also valid up to $X_{NO} = 0.2$ within ± 2 percent.

The corresponding change in the standard free energy for the limiting case is

$$\Delta G^\circ = -RT \ln K'' = -911.5 + 29.19T \tag{23}$$

where $\Delta H^\circ = -911.5$ cal/mol, and $\Delta S^\circ = -29.19$ cal/mol $^\circ K$.

IV. COMPARISON OF AVAILABLE DATA

During the past 30 years numerous investigators have studied various aspects of the N_2O_4-NO system. Verhoek and Daniels (Ref. 5) investigated the dissociation constants of N_2O_4 and of N_2O_3. Giauque and Kemp (Ref. 6) measured the entropy of N_2O_4 and NO_2 and the equilibria in $N_2O_4(g)$ $\rightleftharpoons 2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$. Whittaker, et al., (Ref. 7) investigated the vapor pressure and freezing points of the system, N_2O_4-NO in the composition range 0 to 16.85 percent by weight of NO and in the temperature range -40 to +15°C. Beattie, et al., (Refs. 8-11) made a series of investigations on N_2O_3. They studied the stability of N_2O_3 in the gaseous phase and reported equilibrium constants for the reaction $N_2O_3(g) \rightleftharpoons NO(g) + NO_2(g)$ at 5, 15, 25, 35 and 45°C (Ref. 8). They reported freezing-point data for the NO_2-N_2O_3 system and pure N_2O_3 (Ref. 9). They measured the vapor pressure of mixtures of NO_2 and NO and expressed their results as

$$\log_{10} P \text{ (pressure in mm)} = 8.95 - \frac{f(X)}{T}$$

where $f(X)$ is a function dependent only on the composition of the mixture (Ref. 10). They also determined the composition of the vapor in equilibrium with liquid mixtures of NO_2 and NO (Ref. 11). They found that the vapor in equilibrium with a liquid containing equimolar amounts of NO_2 and NO is almost exclusively NO and that the composition of the vapor above liquid mixtures of NO and NO_2 is nearly independent of temperature for a particular liquid composition.

The results of this investigation are compared in Table 5 and in Fig. 6 with those of other investigations. Both Whittaker, et al., and Beattie, et al., reported their measurements as total pressure vs composition. Whittaker, et al., expressed their composition of liquid phase as the weight percent of NO, and Beattie, et al., as a function of the quantity y_1 in the

Investigator	Wt % NO in liq.	x_{NO}	y_1	Total Pressure, mm Hg at		
				-11.03°C	0°C	25 °C
Whittaker, et al.	2.89	0.087	1.954	163.3	306.3	1083
	5.55	0.155	1.915	198.4	363.2	1268
	8.30	0.220	1.875	229.6	419.5	1458
	10.67	0.270	1.843	256.4	471.0	1655
	14.11	0.336	1.798	309.2	557.1	1881
	16.85	0.384	1.763	353.7	636.6	2146
Beattie, et al.		0	2.000	140.5	264.5	932.8
		0.180	1.900	210.5	389.9	1331
		0.333	1.800	301.8	550.8	1826
		0.464	1.700	472.3	846.6	2708
		0.575	1.600	814.3	1428.0	
		0.623	1.550	1231.0	2122.0	
		0.646	1.525	1749.0	2973.0	
Authors		0.051	1.974	155.1		
		0.171	1.907	197.3		
		0.280	1.837	249.3		
		0.383	1.763	330.0		
		0.542	1.628	617.0		
		0.081	1.958		311.4	
		0.221	1.876		417.1	
		0.351	1.787		572.3	
		0.465	1.697		829.4	
		0.023				950.5
		0.031	1.985			966.8
		0.110	1.942			1149
		0.155				1260
		0.188	1.896			1352
		0.250	1.857			1546
		0.254				1551

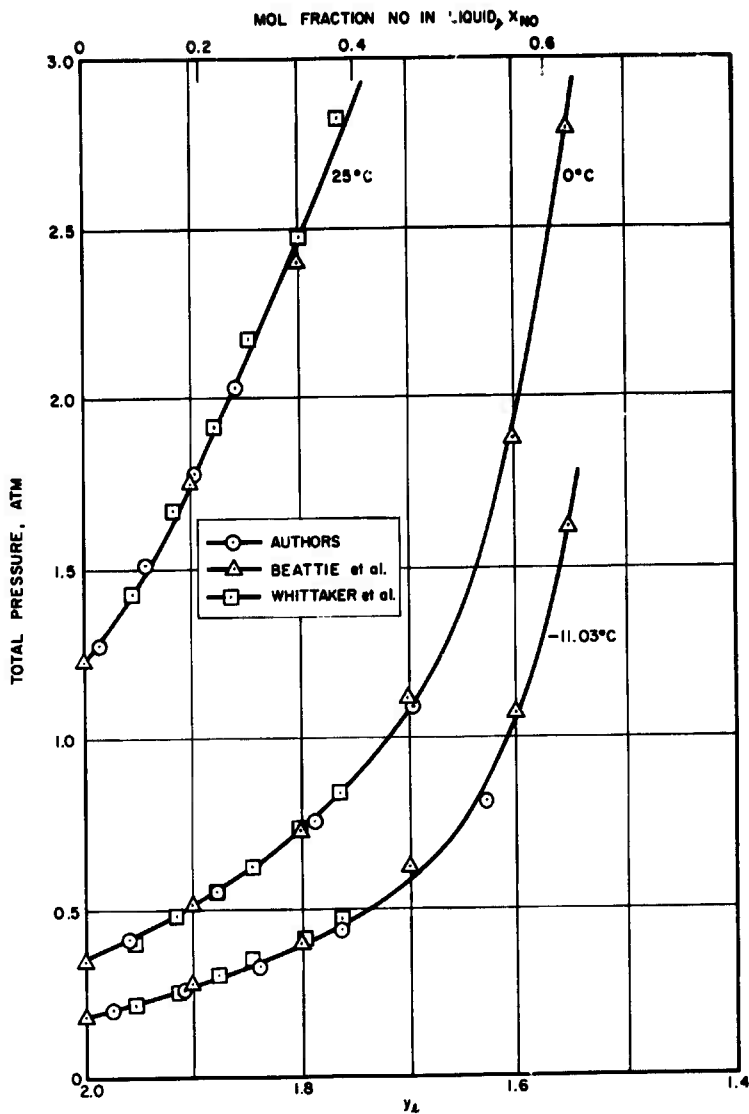Table 5.   Comparison of Available Data

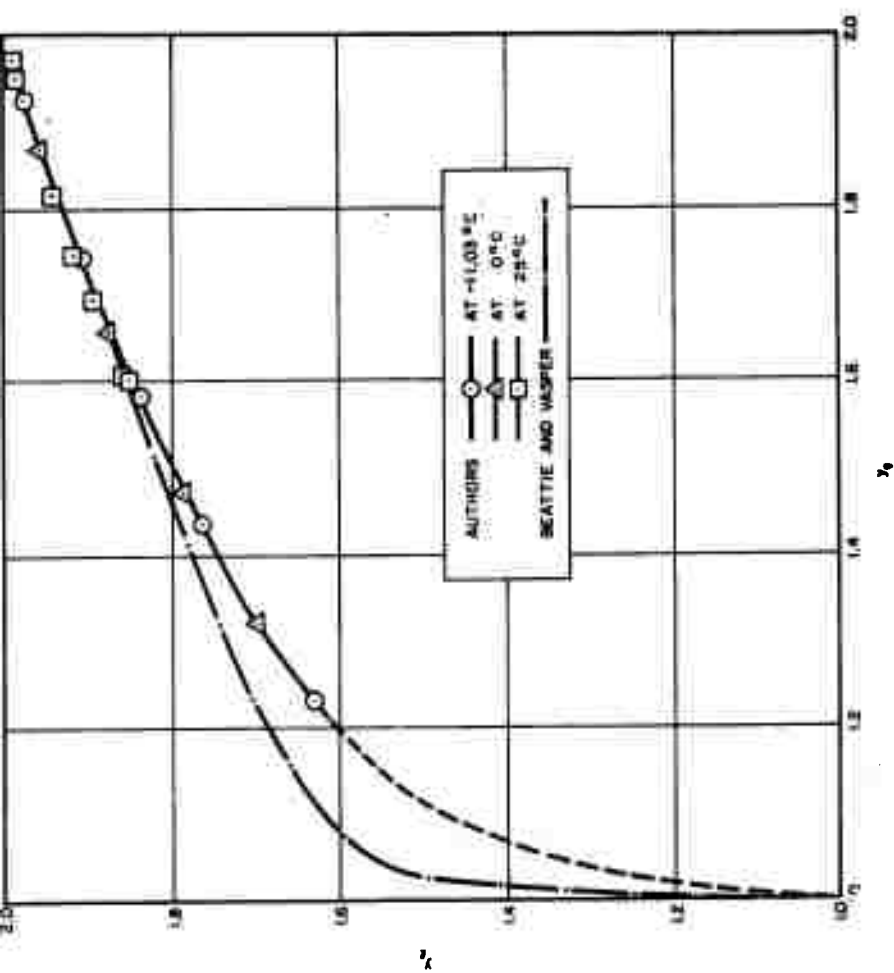Fig. 6. Variation of Total Pressure with O/N = y_1 in Liquid

Fig. 7. Equilibrium Composition in Liquid $O/N = y_l$
and in Gas $O/N = y_g$

formula NO_y in the liquid phase. Therefore all the data were extrapolated
to the same temperature and converted to the common units of total pressure
vs y_1 in Fig. 6. The scale for the mol fraction of NO, X_{NO}, in the liquid
phase, i.e., assuming that in the liquid phase the only species present are
NO and N_2O_4, is also shown in this figure. The agreement among the various
investigations is good at 25, 0, and $-11.03^{\circ}C$ and at pressures less than
2 atm.

Figure 7 is a comparison of the authors' data with those of Beattie
et al., showing the equilibrium composition of the vapor y_g vs the composi-
tion of the liquid y_1 for mixtures of NO and N_2O_4; y_g and y_1 are as indi-
cated before, in terms of the formula NO_y in the gas and liquid phases,
respectively. The authors' data for Fig. 7 (Table 4) are in agreement with
the extrapolated values of Beattie, et al., when the concentration of NO is
low, i.e., y is close to 2 and poor at high NO concentrations. It appears
from these results that the composition of the vapor is nearly independent
of temperature for a given liquid composition, in agreement with the conclu-
sion of Beattie, et al. The authors' results cover the range that have never
been investigated, i.e., the range of $y_1 = 1.6$ to 2.0 and $y_g = 1.2$ to 2,
whereas Beattie, et al., covered the range $y_1 = 1.5$ to 1.8 and $y_g = 1.0$ to
1.5.

REFERENCES

1. N. A. Gokcen, _Solubility of Methylamines in Hydrazine_, ATN-63(9228)-2, Aerospace Corp., El Segundo, Calif. (16 November 1962).

2. E. T. Chang and N. A. Gokcen, _Solubilities of N2, He, and Ar in Liquid N2O4_, ATN-64(9228)-4, Aerospace Corp., El Segundo, Calif. (20 October 1964).

3. C. M. Steese and A. G. Whittaker, "Spectrophotometric Study of the Liquid-Phase Equilibrium $N_2O_4 \rightleftharpoons 2NO_2$ in Pure Nitrogen Tetroxide," _J. Chem. Phys._ 24, 776(1956).

4. _JANAF Thermochemical Tables_, The Dow Chemical Co., Midland, Mich. (1964).

5. F. H. Verhoek and F. Daniels, "The Dissociation Constants of Nitrogen Tetroxide and of Nitrogen Trioxide," _J. Am. Chem. Soc._ 53, 1250 (1931).

6. W. F. Giauque and J. D. Kemp, "The Entropies of Nitrogen Tetroxide and Nitrogen Dioxide. The heat capacity from $15^\circ K$ to the Boiling Point. The Heat of Vaporization and Vapor Pressure. The Equilibria $N_2O_4 = 2NO_2 = 2NO + O_2$," _J. Chem. Phys._ 6, 40 (1938).

7. A. G. Whittaker, R. W. Sprague, S. Skolnik, and G. B. L. Smith, "Vapor Pressures and Freezing Points of the System Nitrogen Tetroxide-Nitric Oxide," _J. Am. Chem. Soc._ 74, 4794 (1952).

8. I. R. Beattie and S. W. Bell, "Dinitrogen Trioxide. Part I. Stability in the Gaseous Phase," _J. Chem. Soc._ 1681 (1957).

9. I. R. Beattie, S. W. Bell, and A. J. Vosper, "Dinitrogen Trioxide. Part II. Freezing-point Data in the System Nitrogen Dioxide-Dinitrogen Trioxide. The Freezing Point of Pure Dinitrogen Trioxide," _J. Chem. Soc._ 4796 (1960).

10. I. R. Beattie, and A. J. Vosper, "Dinitrogen Trioxide. Part III. The Vapor Pressure of Mixtures of Nitrogen Dioxide and Nitric Oxide," _J. Chem. Soc._ 4799 (1960).

11. I. R. Beattie and A. J. Vosper, "Dinitrogen Trioxide. Part IV. Composition of the Vapor in Equilibrium with Liquid Mixture of Nitrogen Dioxide and Nitric Oxide," _J. Chem. Soc._ 2106 (1961).

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The solubilities of O_2, NO, and N_2O_3 in liquid N_2O_4 have been measured over a wide pressure range at -11.03, 0.0, and 25°C. The results show, conclusively, that Henry's law is obeyed for all pressures at each temperature for O_2 and at low pressures for NO and N_2O_3. The standard free energy, enthalpy, and entropy of solution for each gas have been computed.

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