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VISCOSITY OF THE NITRIC OXIDE-NITROGEN DIOXIDE SYSTEM
IN THE LIQUID PHASE

and

EXPERIMENTAL VISCOSITY MEASUREMENTS FOR THE LIQUID
PHASE OF THE NITRIC OXIDE AND NITROGEN DIOXIDE SYSTEM
(ADI)

October, 1953

CHEMICAL ENGINEERING LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

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VISCOSITY OF THE NITRIC OXIDE-NITROGEN DIOXIDE SYSTEM IN THE LIQUID PHASE

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ABSTRACT

No information appears to be available concerning the viscosity of mixtures of nitric oxide and nitrogen dioxide. These oxides are frequently encountered in industrial process fluids. In order to permit the momentum transfer characteristics of the liquid phase of these mixtures to be predicted, viscosity measurements were made.

Viscosity of the liquid phase was measured in the temperature interval between 40° and 280°F. for pressures up to 5,000 pounds per square inch. Data were obtained upon three mixtures within the composition interval between 0 and 0.3 weight fractions nitric oxide. The measurements were made with a rolling ball viscometer.

The results indicate that the viscosity of the liquid phase is not influenced to a large extent by changes in pressure or composition within the range of conditions investigated. The effect of pressure and temperature upon the viscosity of the liquid phase of these mixtures is in reasonable agreement with available data for the viscosity of pure nitrogen dioxide.

(The abstract is intended for publication in a separate section of the journal.)

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INTRODUCTION

No experimental data for the viscosity of the nitric oxide-nitrogen dioxide system were found. Pure nitrogen dioxide in the liquid phase was investigated by Thorpe and Rodger (20). Scheuer (17) studied the viscosity of this pure compound but his results differ markedly from the measurements of Thorpe and Rodger. Measurements of the viscosity of pure nitrogen dioxide in the liquid phase were made at pressures up to 5,000 pounds per square inch in the temperature interval between 40° and 280° F. (10).

The volumetric and phase behavior of mixtures of nitric oxide and nitrogen dioxide has been described (19). These data extend to pressures in excess of 5,000 pounds per square inch at temperatures from 40° to 340° F. and serve as the basis for the volumetric corrections required to determine the absolute viscosity of this binary system. They are in reasonable agreement with the measurements of Purcell and Cheesman (7) for temperatures at which the two investigations may be compared. Baume and Robert (1) also studied the phase behavior of the nitric oxide-nitrogen dioxide system at temperatures below 68° F. and Wittorf (22) determined the limits of

solubility of nitric oxide in nitrogen dioxide. The effect of pressure and temperature upon the specific volume of nitrogen dioxide was investigated (9, 18) and a review of the available data for this compound was presented.

METHODS AND APPARATUS

The present measurements were made with a rolling ball viscometer of a type proposed by Flowers (3) and developed by Hersey (4, 5). The instrument employed was described in connection with measurements of the viscosity of ammonia (2). This equipment involved a stainless steel tube inclined at an angle of approximately 15° down which a closely fitting steel ball was permitted to roll. The time of traverse of the ball between two sets of three coils located near the ends of the tube was determined electronically. A centrifugal pump was employed to return the ball to the upper end of the tube and to bring the system to a uniform composition and temperature. The exit from the roll tube was closed during measurements of the time of traverse of the ball down the tube.

Roll times were measured with a probable error of 0.2% and the temperature of the roll tube was known, with respect to the international platinum scale, within 0.1° F. Pressures were determined by use of a balance (14) calibrated against the vapor pressure of carbon dioxide at the ice point. The pressure of the fluid within the instrument was established through a balanced aneroid type diaphragm (18) and was known within two pounds per square inch or 0.2%, whichever was the larger measure of uncertainty.

Hydrodynamic characteristics of rolling ball viscometers were investigated by Watson (21), Hersey and Shore (5), and Hubbard and Brown (6) and have been considered in the application of this instrument (2). The apparatus was calibrated with n-pentane in the liquid phase using the critically chosen values of Rossini (11) for the viscosity of this compound at atmospheric pressure. An equation of the following form (2) was used to establish the viscosity from the measured roll time:

$$\eta = A\theta(\sigma_o - \sigma_f) - \frac{B\sigma_f}{\theta} \quad (1)$$

The coefficients A and B were determined from the measured roll times with n-pentane as a function of temperature and were checked with water. Recalibration of the instrument without cleaning the roll tube after completion of the investigation of two of the mixtures of nitric oxide and nitrogen dioxide indicated a change in calibration of less than 0.3%. All measurements reported were carried out at sufficiently low velocities so that the effect of the acceleration of the fluid around the ball was less than 5% of the measured roll time. It is believed that the first order correction for acceleration included in Equation 1 suffices for such hydrodynamic conditions. The viscosities were expressed in micropoises as a result of widespread usage, even though this unit is not dimensionally consistent with the independent variables.

Nitrogen dioxide was first introduced into the apparatus and the roll times were checked at a known temperature. The desired quantity of nitric oxide was then added from a weighing bomb while the apparatus was at a temperature of approximately 40° F. Bubble point pressures of the nitric oxide-nitrogen dioxide system (19) were sufficiently low at this temperature to permit the desired quantities of nitric oxide to be introduced without difficulty. The composition was determined from the weights of the nitric oxide and nitrogen dioxide introduced into the viscometer and was checked by the measured bubble point pressures. In addition, a sample of the liquid phase was withdrawn and its specific weight determined by pycnometer techniques at a known pressure and temperature. The information concerning the volumetric and phase behavior of the nitric oxide-nitrogen dioxide system (19) was employed in order to relate the measured bubble point pressures and specific weights of the liquid phase to composition. The maximum difference between the composition as measured by the different methods was 0.012 weight fraction nitric oxide.

RESULTS

The effect of pressure upon the viscosity of a mixture of nitric oxide and nitrogen dioxide containing 0.991 weight fraction nitrogen dioxide was determined at four temperatures between 40° and 280° F. as a preliminary part of this investigation. The measurements involved rather large standard deviations as compared to later data reported here. The data for

this sample have not been given more than 20% of the weight given to each of the other mixtures investigated. Two mixtures containing 0.920 and 0.774 weight fractions nitrogen dioxide were investigated at five temperatures between 40° and 280° F. The experimental results obtained for the mixture containing 0.920 weight fraction nitrogen dioxide are shown in Figure 1. The detailed experimental measurements for all of the mixtures are available (8). The full curves shown in Figure 1 represent data smoothed with respect to pressure, temperature, and composition. For the two mixtures and nitrogen dioxide (10), the standard deviation of the experimental data from the smoothed curves was 47 micropoises and the average deviation was 3.8 micropoises if regard was taken of sign. If the measurements for the mixture containing 0.991 nitrogen dioxide are included, the standard and average deviations are several times as large.

Values of the viscosity of the liquid phase of this system are reported in Table I for even values of pressure, temperature, and composition. These data include earlier measurements upon the viscosity of nitrogen dioxide (10) which were modified slightly at the lower temperatures on the basis of the present measurements. The standard deviation of 47 micropoises was comparable to that found in the earlier studies of the viscosity of nitrogen dioxide (10).

The influence of composition upon the viscosity of the nitric oxide-nitrogen dioxide system is shown in Figure 2 for each of the temperatures investigated. The solid points represent the data obtained from smoothing the experimental measurements for the individual mixtures, whereas the

full curves correspond to the values recorded in Table I. The reproducibility of the data for an individual composition at a particular time was much better than that found for the entire set of measurements. The viscosity of the liquid phase at bubble point is depicted in Figure 3. The small effect of changes in composition upon the viscosity of the liquid phase is evident. Data recorded in Table I indicate that, within the range of pressures and compositions investigated, the influence of these variables is small. Such behavior is in contradistinction to the marked variations in viscosity with changes in pressure or composition in the case of hydrocarbon systems (12, 13, 15, 16). Pressure and temperature influence the viscosity of mixtures of nitric oxide and nitrogen dioxide to much the same extent as that found for pure nitrogen dioxide (10).

ACKNOWLEDGMENT

This experimental program was supported by the Office of Naval Research. G. N. Richter was the recipient of a Union Carbide and Carbon Corporation graduate fellowship. Betty Kendall carried out the calculations and Elizabeth McLaughlin aided in the assembly of the manuscript. The assistance of W. N. Lacey in its review is acknowledged.

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NOMENCLATURE

A	dimensional coefficient of Equation 1
B	dimensional coefficient of Equation 1
η	absolute viscosity, micropoises
σ_b	specific weight of ball, pounds per cubic foot
σ_f	specific weight of fluid, pounds per cubic foot
θ	roll time of ball, seconds

LIST OF FIGURES

1. **Viscosity of the Liquid Phase of a Mixture Containing 0.920 Weight Fraction Nitrogen Dioxide**
2. **Viscosity-Composition Diagram**
3. **Viscosity of Nitric Oxide-Nitrogen Dioxide System at Bubble Point**

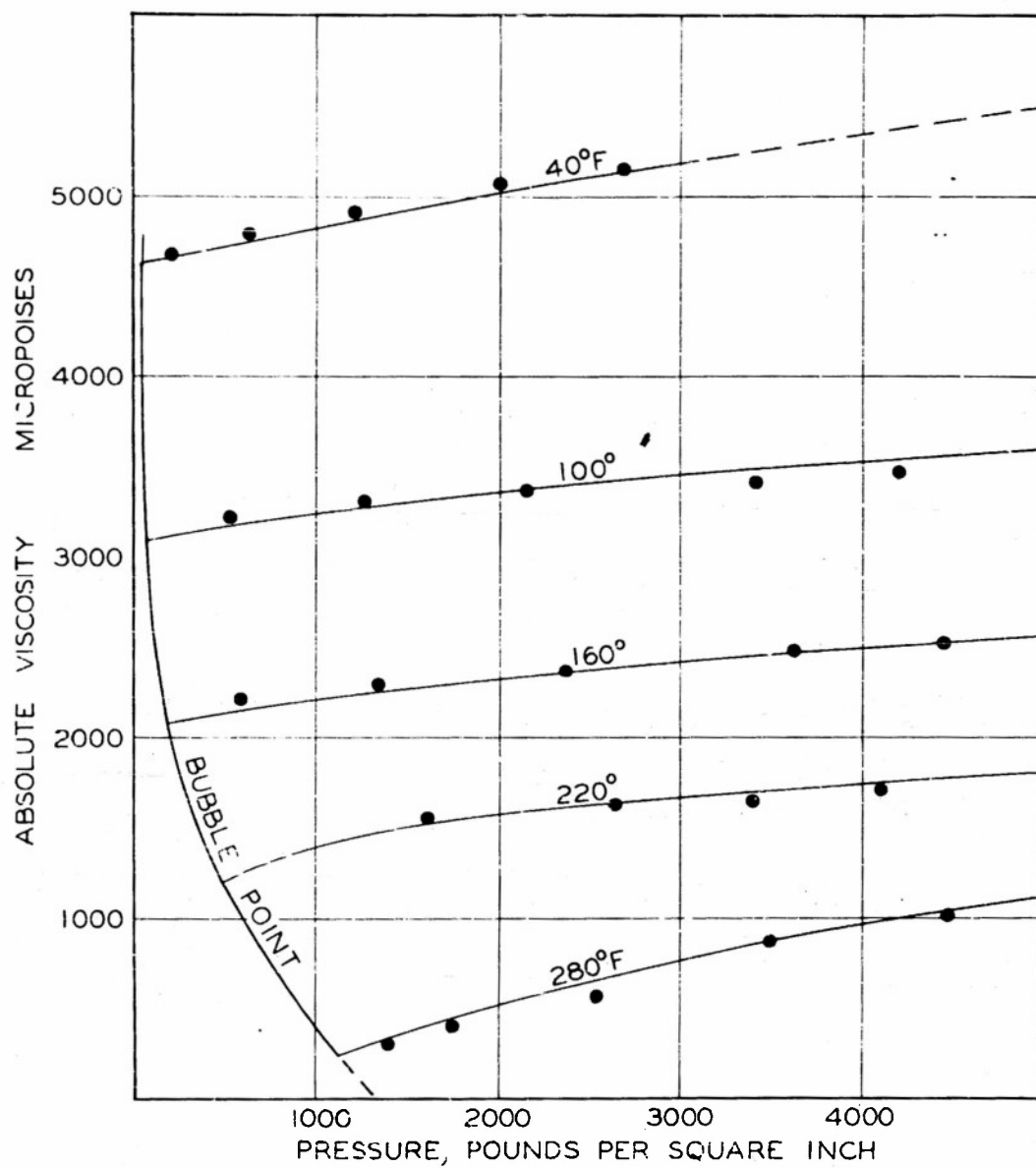


Fig. 1 Viscosity of the Liquid Phase of a Mixture Containing 0.920 Weight Fraction Nitrogen Dioxide

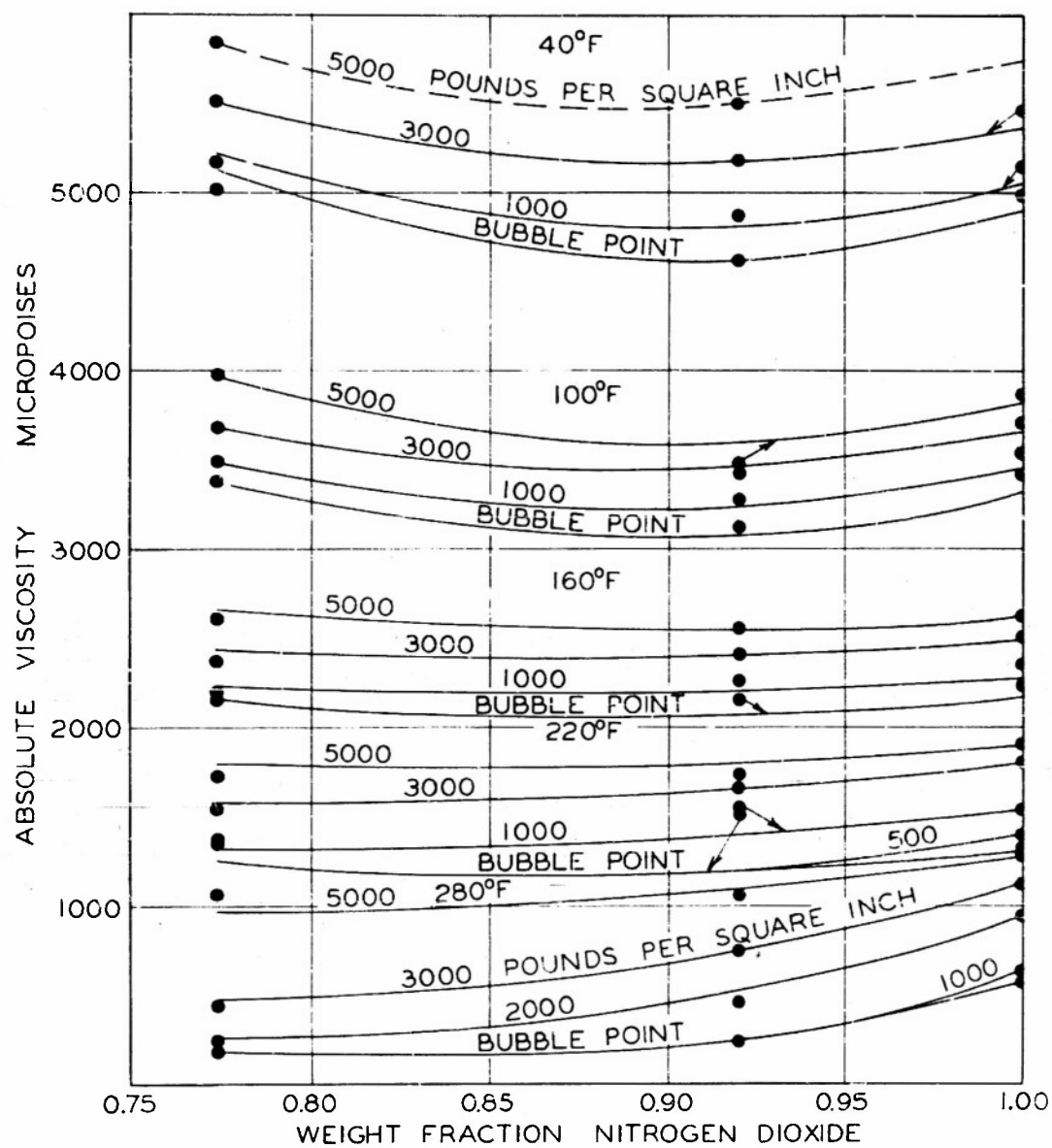


Fig. 2 Viscosity-Composition Diagram

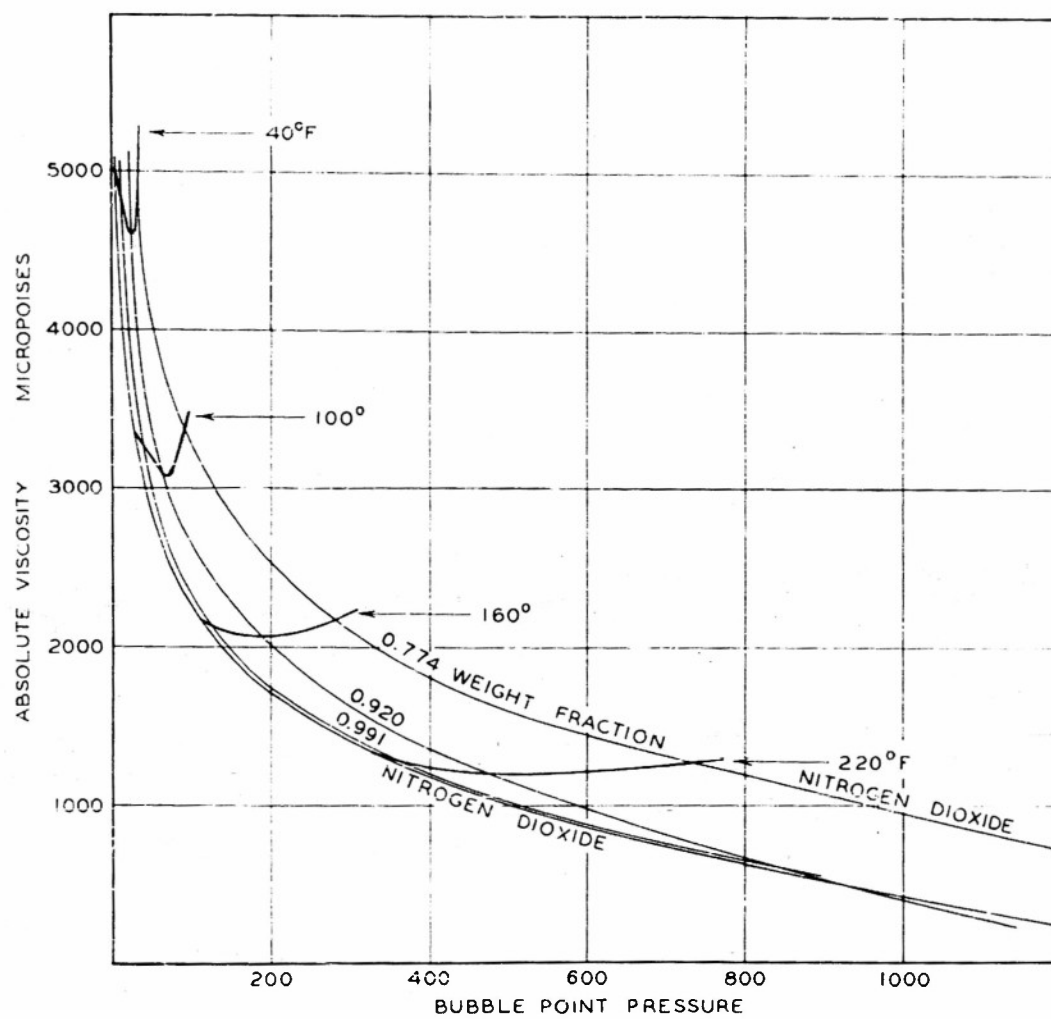


Fig. 3. Viscosity of Nitric Oxide-Nitrogen Dioxide System at Bubble Point

LIST OF TABLES

- 1. Viscosity of Mixtures of Nitric Oxide and Nitrogen Dioxide**

TABLE I

VISCOSITY ^a OF MIXTURES OF NITRIC OXIDE AND NITROGEN DIOXIDE

Pressure Lb. /Sq. In. Absolute	Wt. Frac. Nitrogen Dioxide				
	0.80	0.85	0.90	0.95	1.00
	<u>40 °F.</u>				
Bubble Point	(30) ^b 4960	(29) 4720	(27) 4610	(22) 4680	(6.5) 4900
200	4980	4760	4660	4730	4940
400	5000	4800	4700	4760	4970
600	5030	4830	4740	4800	5020
800	5060	4860	4770	4830	5040
1000	5070	4880	4820	4870	5050
1250	5120	4940	4870	4920	5100
1500	5140	4960	4910	4970	5140
1750	5190	5020	4960	5020	5180
2000	5220	5060	5000	5060	5220
2250	5270	5120	5060	5100	5260
2500	5310	5140	5090	5140	5290
2750	5360	5190	5130	5180	5340
3000	5380	5220	5170	5220	5370
3500	[5470] ^c	[5300]	[5260]	[5320]	[5450]
4000	[5550]	[5380]	[5330]	[5380]	[5530]
4500	[5620]	[5460]	[5420]	[5490]	[5625]
5000	[5680]	[5510]	[5480]	[5580]	[5740]
	<u>100 °F.</u>				
Bubble Point	(86) 3260	(79) 3120	(71) 3070	(60) 3120	(31) 3320
200	3300	3200	3100	3200	3400
400	3300	3200	3100	3200	3400
600	3340	3200	3170	3240	3410
800	3360	3230	3200	3270	3430
1000	3380	3260	3220	3300	3450

a Viscosity expressed in micropoises.

b Figures in parentheses represent bubble point pressures expressed in pounds per square inch absolute.

c Figures in brackets were obtained by extrapolation.

TABLE I cont.

Pressure Lb. /Sq. In. Absolute	Wt. Frac. Nitrogen Dioxide				
	0.80	0.85	0.90	0.95	1.00
Bubble Point	(86) 3260	(79) 3120	(71) 3070	(60) 3120	(31) 3320
1250	3410	3300	3260	3320	3480
1500	3440	3330	3280	3350	3510
1750	3470	3350	3310	3390	3540
2000	3500	3380	3350	3420	3560
2250	3520	3400	3370	3440	3580
2500	3550	3440	3400	3480	3620
2750	3560	3500	3420	3500	3640
3000	3580	3580	3440	3520	3660
3500	3630	3510	3480	3560	3700
4000	3690	3540	3500	3580	3740
4500	3760	3600	3550	3620	3780
5000	3840	3660	3580	3660	3820
160 °F.					
Bubble Point	(270) 2110	(239) 2070	(204) 2080	(162) 2090	(111) 2170
200	--	--	--	2100	2200
400	2200	2100	2100	2100	2200
600	2200	2100	2100	2180	2230
800	2200	2180	2180	2200	2260
1000	2220	2200	2210	2240	2280
1250	2250	2240	2240	2260	2310
1500	2270	2260	2270	2290	2340
1750	2300	2280	2290	2320	2360
2000	2320	2310	2320	2340	2380
2250	2340	2320	2330	2360	2400
2500	2360	2350	2360	2380	2430
2750	2390	2370	2370	2400	2460
3000	2420	2400	2410	2440	2480
3500	2470	2460	2460	2470	2540
4000	2520	2490	2490	2500	2580
4500	2570	2540	2530	2540	2600
5000	2620	2580	2560	2570	2620

TABLE I cont.

Pressure Lb. /Sq. In. Absolute	Wt. Frac. Nitrogen Dioxide				
	0.80	0.85	0.90	0.95	1.00
<u>220 °F.</u>					
Bubble Point	(701) 1220	(610) 1180	(516) 1190	(424) 1220	(333) 1320
200	--	--	--	--	--
400	--	--	--	--	1400
600	--	--	1240	1310	1420
800	1280	1280	1310	1370	1480
1000	1320	1340	1380	1440	1540
1250	1360	1380	1430	1510	1600
1500	1400	1420	1480	1550	1650
1750	1440	1460	1520	1600	1680
2000	1480	1500	1560	1630	1720
2250	1510	1530	1580	1660	1740
2500	1520	1550	1590	1660	1760
2750	1560	1600	1620	1690	1780
3000	1590	1620	1640	1700	1800
3500	1630	1640	1680	1740	1820
4000	1680	1690	1720	1780	1850
4500	1740	1740	1760	1820	1880
5000	1790	1780	1780	1830	1900
<u>280 °F.</u>					
Bubble Point	(1570) 160	(1388) 160	(1201) 200	(1026) 340	(864) 570
200	--	--	--	--	--
400	--	--	--	--	--
600	--	--	--	--	--
800	--	--	--	--	--
1000	--	--	--	--	630
1250	--	--	220	410	710
1500	--	180	290	490	800
1750	220	260	360	580	880
2000	270	320	450	650	940
2250	340	400	520	720	990
2500	390	450	570	770	1040

TABLE I cont.

Pressure Lb. /Sq. In. Absolute	Wt. Frac. Nitrogen Dioxide				
	0.80	0.85	0.90	0.95	1.00
Bubble Point	(1570)	(1388)	(1201)	(1026)	(864)
	160	160	200	340	570
2750	450	520	640	830	1090
3000	500	560	690	880	1120
3500	620	690	810	980	1170
4000	750	800	910	1040	1210
4500	880	920	1000	1110	1250
5000	980	1010	1080	1160	1280

**EXPERIMENTAL VISCOSITY MEASUREMENTS FOR THE LIQUID
PHASE OF THE NITRIC OXIDE AND NITROGEN DIOXIDE SYSTEM**

Supplemental to

**VISCOSITY OF THE NITRIC OXIDE-NITROGEN DIOXIDE SYSTEM
IN THE LIQUID PHASE**

**This supplemental material will be deposited
with the American Documentation Institute, Library
of Congress, Washington, D. C., from which micro-
film or photostats may be obtained upon request.**

**Chemical Engineering Laboratory
California Institute of Technology
Pasadena, California**

October, 1953

EXPERIMENTAL VISCOSITY MEASUREMENTS FOR THE LIQUID PHASE OF THE NITRIC OXIDE AND NITROGEN DIOXIDE SYSTEM

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Viscosity of the liquid phase for mixtures involving nitric oxide and nitrogen dioxide was measured at pressures up to 5,000 pounds per square inch for five temperatures between 40° and 280° F. (1). These measurements supplement studies of the viscosity of liquid nitrogen dioxide (2). The data were obtained by means of a rolling ball viscometer (3). The methods of calibration and the details of the equipment are available (2, 3). Temperatures of the viscometer were known within 0.1° F. of the international platinum scale and pressures with a probable error of 0.2% or two pounds per square inch, whichever was the larger uncertainty. Roll times were measured with a probable error of 0.03 second. The instrument was calibrated with n-pentane liquid in the laminar region and with air and carbon dioxide in the turbulent region (3). No measurements of the nitric oxide-nitrogen dioxide system were made in the turbulent region.

Table I records the experimental measurements of viscosity for this binary system for three different mixtures containing 0.774, 0.920, and 0.991 weight fractions nitrogen dioxide. The absolute viscosities

recorded were calculated from at least three roll times at each state. The average deviation from the mean of these three roll times was less than 0.02 second. The calibration of the instrument in the case of the mixtures containing 0.991 weight fraction nitrogen dioxide changed by 1.4% during the course of the measurements. This variation was distributed over the five temperatures in a linear fashion. It is believed that the studies of the mixtures containing 0.991 weight fraction nitrogen dioxide are somewhat less reliable than the results obtained for the other two mixtures. In the case of the two mixtures containing 0.774 and 0.920 weight fractions nitrogen dioxide the calibration changed by less than the probable error of measurement. The results for these two mixtures and for pure nitrogen dioxide involve a standard deviation in the smoothed viscosity of 47 micropoises considering all the uncertainty to be in the viscosity and none in the pressure, temperature, or composition. On the other hand, a probable error of 122 micropoises was found if the data for 0.991 weight fraction nitrogen dioxide were included.

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- I. Experimental Measurements of Viscosity of Nitric Oxide and Nitrogen Dioxide in the Liquid Phase**

TABLE I EXPERIMENTAL MEASUREMENTS OF VISCOSITY OF NITRIC OXIDE AND NITROGEN DIOXIDE IN THE LIQUID PHASE

Pressure Lb./Sq. In. Absolute	Average Roll Time, Second	Absolute Viscosity, Micropoise	Pressure Lb./Sq. In. Absolute	Average Roll Time, Second	Absolute Viscosity, Micropoise	Pressure Lb./Sq. In. Absolute	Average Roll Time, Second	Absolute Viscosity, Micropoise
Wt. Frac. Nitrogen Dioxide 0.774								
40 °F.								
230	43.98	5005	212	43.20	4677	53	43.77	4738
628	44.44	5103	629	43.66	4779	440	43.57	4670
1109	44.87	5189	1221	44.28	4918	1224	44.15	4798
2128	45.66	5341	2001	44.98	5070	1852	44.72	4923
2910	46.47	5512	2688	45.39	5147			
100 °F.								
407	36.96	3417	530	36.74	3218	320	36.62	3070
1294	37.55	3509	1270	37.15	3302	1038	36.97	3149
2215	38.04	3597	2158	37.56	3371	3644	38.21	3372
3427	38.73	3747	3417	37.86	3405	4522	38.57	3443
4214	39.25	3843	4211	38.20	3466			
160 °F.								
650	31.76	2185	585	32.14	2205	640	32.11	2037
1314	32.04	2222	1342	32.60	2291	1298	32.48	2106
2211	32.52	2315	2370	33.08	2372	2164	32.81	2158
3499	33.09	2417	3627	33.67	2480	3110	33.23	2227
4426	33.66	2543	4450	33.97	2529	3964	33.52	2279
220 °F.								
1104	27.76	1370	1608	28.93	1554	713	28.66	1377
1734	28.19	1437	2640	29.44	1624	1535	29.21	1467
2455	28.60	1498	3399	29.74	1650	2597	29.37	1415
3467	29.17	1598	4103	30.09	1707	3534	29.85	1491
4439	29.62	1676				4400	30.12	1516
280 °F.								
1809	21.96	189	1408	22.86	300			
2404	23.06	320	1768	23.48	404			
3063	23.86	454	2539	24.50	574			
3877	24.89	692	3496	25.81	862			
4626	25.79	909	4480	26.63	1012			