

Viscosity of the $\text{N}_2\text{O}_4\text{--NO}_2$ Gas System

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The viscosity of the equilibrium gaseous $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ system was measured in the temperature range 25° to 170° C. at pressures from 0.5 to 5 atm. employing a rolling-ball viscometer. The behavior of viscosity of this system reveals the dependence of chemical composition on temperature and pressure.

THE VISCOSITY of the equilibrium gaseous system $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ (herein for brevity called NO_2) was measured in the temperature range 25° to 170° C. at pressures from 0.5 to 5 atm. employing a rolling-ball viscometer. The theory of the rolling-ball viscometer is discussed in detail by Hubbard and Brown (6). A critical analysis of falling- and rolling-ball viscometers and of the falling-cylinder viscometer is made by Lohrenz and Kurata (8). The theory for the rolling-ball viscometer in the region of laminar flow around the ball leads to the following simple expression for μ , the viscosity of the fluid, and θ , the roll time:

$$\mu = a_1(\rho_b - \rho_g)\theta + a_2 \quad (1)$$

ρ_b and ρ_g are densities of the ball material and gas respectively and a_1 and a_2 are constants characteristic of the viscometer that are determined by calibration with fluids of known viscosity. Calibration was performed using both air and CO_2 at pressures near one atm. and at temperatures in the range 25° to 150° C., values of viscosity being taken from Keyes (7). Over this temperature span, viscosities of the calibrating gases were in the range of viscosities for NO_2 gas. The value of a_1 was 2.147×10^{-6} (poises cc./sec. g.) and a_2 was 16.4×10^{-6} poise. The density of the glass ball, ρ_b was 2.2139 g./cc. at 20° C. and the density of NO_2 gas, ρ_g was taken from the data of Reamer and Sage (9).

EXPERIMENTAL

The viscometer assembly is shown schematically in Figure 1. Oxygen was bubbled through commercially pure liquid NO_2 (99.5 wt. % NO_2) to oxidize any traces of NO present, and the resulting NO_2 vapor was then condensed. The liquid was fractionally distilled into the ampoule shown in Figure 1 where it was frozen. The solid was pure white indicating absence of NO (or N_2O_3). The tip of the evacuated ampoule was fused after loading. The ampoule was equipped with an arm containing a glass break seal which could be broken when desired by a magnetically driven iron bar enclosed in glass allowing the NO_2 access to the rest of the thoroughly evacuated system. After the break-seal was broken the NO_2 in the ampoule was warmed and the double U-tube cooled with ice-water so that liquid NO_2 could be

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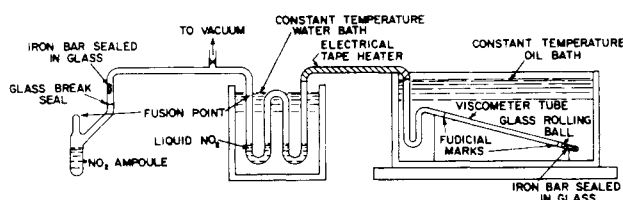


Figure 1. Schematic diagram of viscometer assembly

collected in the U-tubes. When the U-tubes were filled with the desired amount of NO_2 the ampoule was removed by fusing the glass near the entrance to the constant temperature water bath.

By controlling the temperature of the water bath the vapor pressure of the liquid NO_2 and thus the NO_2 pressure in the viscometer was established. The pressure of NO_2 was not measured directly but was obtained from the knowledge of the temperature of the liquid employing vapor pressure data of Schlinger and Sage (10). The temperature of the viscometer was always higher than that of the water bath to prevent condensation in the viscometer tube. The interconnecting line between the oil bath and water bath was wrapped with an electrical tape heater to prevent condensation. The U-bend upstream of the viscometer tube was provided to add length of tubing and thus help eliminate temperature or concentration gradients in the viscometer tube proper. Temperatures in both baths were controlled to within 0.05° C.

For calibration runs air was carefully dried passing it through a bed of MgClO_4 , and CO_2 gas was obtained by subliming it from solid CO_2 . Each gas was introduced to the evacuated system via the vacuum line manifold. The pressure of the gas was measured with a mercury filled manometer.

The viscometer tube was precision bore borosilicate glass with a nominal internal diameter of 0.121 inches with a length of about 12 inches between fiducial marks. The carefully ground spherical glass ball was 0.12067 ± 0.00002 inches in diameter. The viscometer-bath assembly could be leveled by means of leveling screws and spirit levels. The viscometer tube lay at an angle of about 15° with the horizontal and was supported by a block containing a V-groove in the top. Before a viscosity run the glass ball was pushed up beyond the upper fiducial mark by the glass-enclosed iron bar which was translated by manually sliding an externally located horseshoe magnet along the tube. The iron bar was returned quickly to the bottom of the tube by the magnet and due to the close tolerance between the tube and ball, the ball rolled very slowly so that any disturbance in the fluid caused by the rod should have been damped out by the time the ball passed the upper fiducial mark. In each calibration run with air and CO_2 as well as runs with NO_2 the roll time for each set of conditions was repeated at least five times. For the whole set of runs the roll times ranged between about 24 and 46 seconds with a reproducibility in roll time of $\pm 0.3\%$ or better.

RESULTS

The viscosity data for NO_2 gas are shown in Table I and Figure 2. For comparison in Figure 2 experimental data of Beer (1) and of Thievon, Sterbutzel, and Beal (11) as well as theoretical data of Brokaw (3) are included. Agreement is fairly good, except for the data of Thievon and coworkers and the disagreement of the latter data is not understood.

Table I. Absolute Viscosity of NO₂ Gas (Micropoise)

Temp., ° C.	Pressure (Atm.)				
	0.5	1.0	2.0	3.0	5.0
25	135.5	132.5			
30	140.0	136.3			
40	149.7	144.5	140.0		
50	159.8	153.5	147.8	145.0	
60	169.8	163.3	157.5	154.3	
70	178.1	173.0	167.2	163.8	158.3
80	185.3	182.4	177.5	173.5	168.1
90	191.8	190.8	186.7	183.6	178.8
100	197.9	197.9	195.3	193.0	189.0
110	203.3	203.9	202.3	199.7	197.4
120	208.3	209.4	208.2	207.1	204.7
130	212.8	214.3	214.0	213.2	211.4
140	217.3	218.8	219.3	218.7	217.5
150	221.8	223.5	224.4	223.5	222.9
160	226.4	228.2	229.1	228.1	227.7
170	230.9	232.7	233.0	232.6	232.3

In ordinary nonreacting gases as the pressure is increased the viscosity increases as depicted by the law of corresponding states chart of Carr, Kobayashi, and Burroughs (4). From the data of Gray and Yoffe (5) the critical pressure of NO₂ gas is 99.96 atm. and the critical temperature is 158.2° C. The highest pressure in these measurements, 5 atm., corresponds to a reduced pressure of about 0.05, and for this low a value of reduced pressure the effect of pressure on viscosity is small for reduced temperatures in the range of about 0.7 to 1.1 encountered in this study. The fact that the viscosity decreases with increase in pressure below 100° C. as seen in Figure 2, can be qualitatively explained by the fact that the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$ shifts to the left with increase in pressure increasing the concentration of the less viscous species N₂O₄. From the Lennard-Jones parameters for the N₂O₄ and NO₂ species assumed by Brokaw (3) and employing the method of Bird, Stewart, and Lightfoot (2) for calculating viscosity it is found that: $\mu_{N_2O_4}/\mu_{NO_2}$ is close to 0.75 in the temperature range 25° C. to 150° C. The behavior of the data above 100° C. where some of the isobaric curves crossover one another is unexplained. The tendency for an increase in pressure to result in an increased viscosity may overshadow the effect on reducing viscosity of shift in equilibrium at elevated temperatures where the fraction of N₂O₄ dissociated to NO₂ approaches unity.

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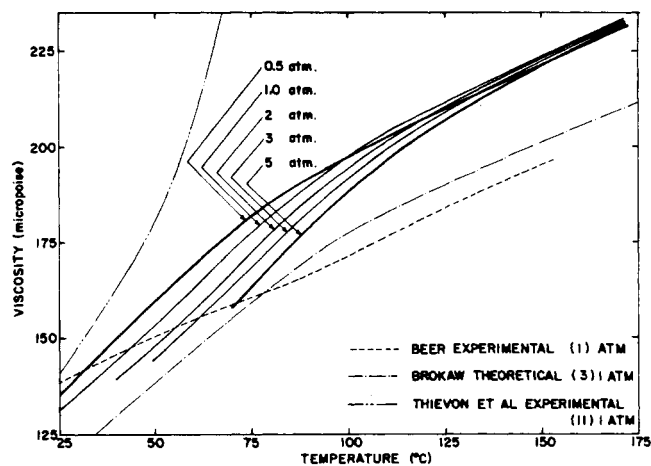


Figure 2. Viscosity of NO₂ gas as a function of temperature and pressure

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