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SOME STUDIES OF THE OXIDES OF NITROGEN

ROGERS, E.; SAGE, B.H.; JAN^o52 3PP PHOTO, GRAPHS

OXIDANTS - PERFORMANCE
NITROGEN OXIDES

FUELS AND LUBRICANTS (12)
FLUID PROPELLANTS (7)

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Some Studies of the Oxides of Nitrogen

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Some Studies of the Oxides of Nitrogen

The search for satisfactory oxidizing components for binary liquid propellant systems has been the subject of much investigation. The oxides of nitrogen are possible oxidants for such liquid fuel systems. In order to permit a better understanding of the behavior of these oxides in propellant systems, a series of measurements of the physical properties and the phase behavior of nitrogen dioxide, nitric oxide, and their mixtures have been made. The present work is directed to an evaluation of the specific volume, thermal conductivity, and viscosity of the liquid phase of nitrogen dioxide and its mixtures with nitric oxide. In addition, the specific volume of the gas phase has been established. The measurements were carried out in the constant-volume, spherical container shown in Fig. 1, at pressures up to 7000 pounds per square inch (psi) in the temperature interval between 40° and 340° F. The desired quantities of nitrogen dioxide or mixtures of this compound with nitric oxide were added to the vessel and the equilibrium pressure was determined at a series of temperatures.

This article by E. Rogers and B. H. Sage of the California Institute of Technology describes some of the work done under contract with ONR's Chemistry Branch (Project NR-058-007). The work is directed toward a better understanding of nitrogen oxide and its mixture with nitric oxide, components for binary liquid propellant systems.

The oxides of nitrogen are interesting inorganic chemical compounds and have been studied extensively (1,2). In the case of nitrogen dioxide, an increase in pressure favors the formation of a dimeric molecule (nitrogen tetroxide) from two molecules of nitrogen dioxide. The chemical equilibrium between the two forms of this oxide of nitrogen has been investigated (3), and it appears that nitrogen dioxide is the predominant component in the gas phase at low pressures and elevated temperatures.

This predominance is shown in Fig. 2 where the compressibility factor, the ratio of the specific volume of the actual gas to that of a perfect gas, is presented for nitrogen dioxide. In the single-phase region, the compressibility factor approaches unity as the pressure is decreased. In the case of the dew point gas, even at relatively low pressures the compressibility factor appears to approach 0.5 rather than unity, thus indicating that the molecular weight of the gas under these conditions is nearly twice that of nitrogen dioxide. Agreement of these values with earlier measurements is satisfactory (4,5). For a pure substance it is unusual that the saturated gas becomes more nearly a perfect gas as the temperature increases. At low temperatures there is but little change in vapor pressure with temperature. Therefore

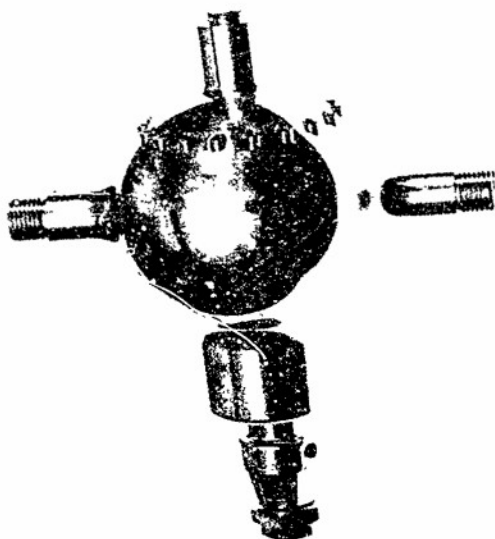


Fig. 1. Spherical equilibrium vessel

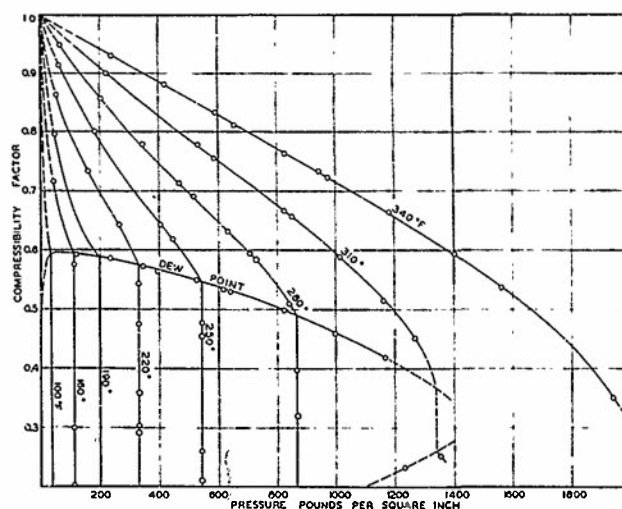


Fig. 2. Compressibility factor for nitrogen dioxide (Ind. Eng. Chem.)

the effect of increased pressure which tends to drive the chemical equilibrium towards the nitrogen tetroxide is overshadowed by the increase in temperature which favors the formation of nitrogen dioxide. This effect is reversed at the higher temperatures where the influence of pressure becomes of controlling importance. Thus the compressibility factor of the saturated gas first increases, then decreases with a progressive rise in temperature. The deviation of nitrogen dioxide (i.e., the equilibrium mixture of oxide) from perfect gas behavior with an increase in pressure in the single-phase region follows normal generalizations.

Fig. 3 depicts the specific volume of liquid nitrogen dioxide as functions of pressure and temperature. The behavior shown in this diagram is similar to that found for other compounds. None of the anomalies which were

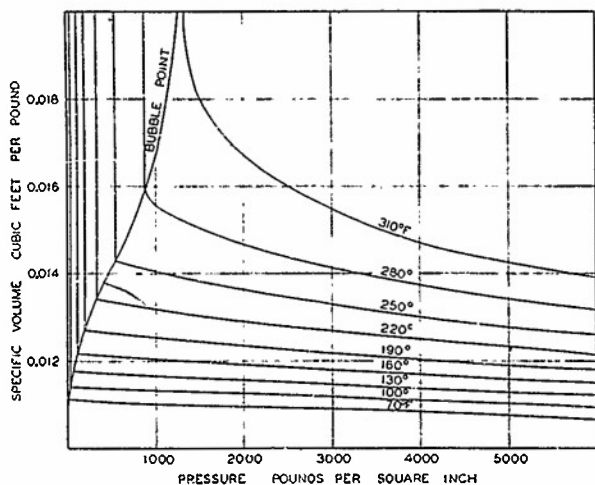


Fig. 3. Specific volume of liquid nitrogen dioxide (Ind. Eng. Chem.)

discussed in connection with the behavior of the saturated gas is present in the case of the liquid. Fig. 4 presents the vapor pressure of nitrogen dioxide. Good agreement exists between the several sets of measurements (4,6,7). Under conditions usually encountered in the field, the vapor pressure of nitrogen dioxide will remain below 100 psi.

One of the possible disadvantages of nitrogen dioxide as an oxidant is its relatively high freezing point. Nitric oxide dissolved in nitrogen dioxide will decrease materially the freezing point of the latter compound, even below -40° F by 20 wt -% of nitric oxide. This may be a satisfactory means of overcoming one of the limitations of nitrogen dioxide as an oxidant.

The solution of nitric oxide in nitrogen dioxide causes an increase in the two-phase

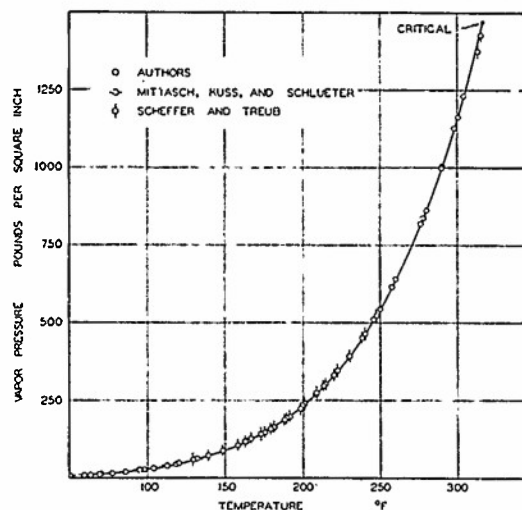


Fig. 4. Vapor pressure of nitrogen dioxide

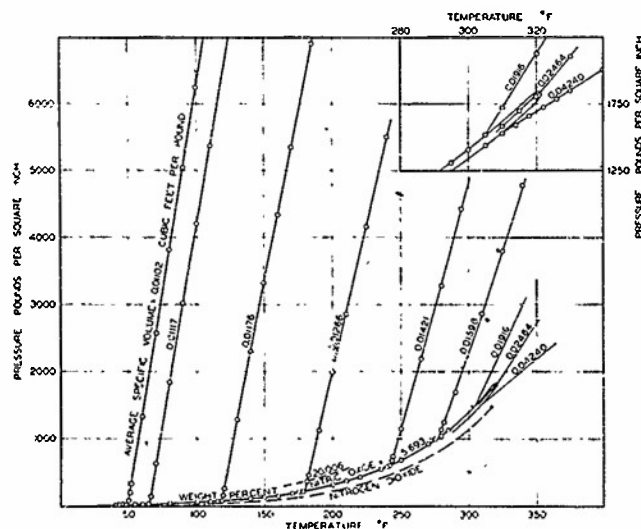


Fig. 5. Effect of nitric oxide on bubble point pressure of mixture with nitrogen dioxide.

pressure. Fig. 5 depicts estimates of the effect of nitric oxide upon the bubble point pressure of mixtures with nitrogen dioxide; 20 wt.-% nitric oxide increases the bubble point pressure of the system to 445 psi at 190° F. The vapor pressure of pure nitrogen dioxide at this temperature is about 196 psi. These data serve to show that only a relatively small increase in the two-phase pressure is involved in obtaining a marked effect in lowering the freezing point by adding nitric oxide.

The properties of nitric oxide were also studied in some detail (1). This compound is much more nearly a perfect gas than nitrogen dioxide. Fig. 6 shows the compressibility factor of nitric oxide (8) as functions of pressure for several temperatures. This material deviates only about 5% from the behavior of a perfect gas at pressures up to 2500 psi at a temperature of 100° F. The marked difference in the characteristics in the two oxides of nitrogen is evident from a comparison of Figs. 2 and 6.

Neither nitrogen dioxide nor nitric oxide undergoes significant decomposition when stored

in mild steel containers. The nitrogen dioxide and its mixtures with nitric oxide are relatively active oxidants and apparently play an important part in the nitration of many organic compounds (2,9). For this reason they should be considered as useful additions to the series of compounds which may be employed as the oxidant in binary liquid fuel systems despite their toxicity.

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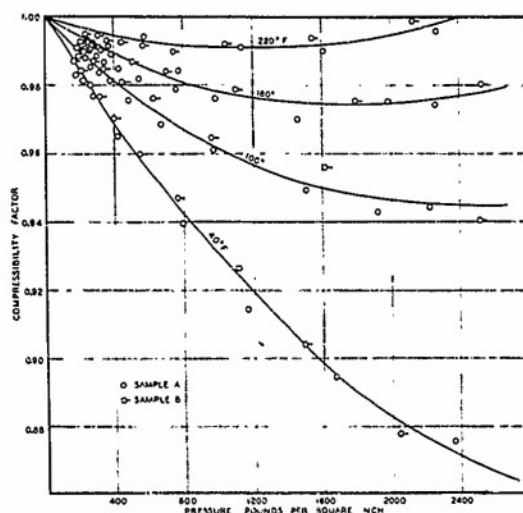


Fig. 6. Compressibility factor of nitric oxide as related to pressure for several temperatures (Ind. Eng. Chem.)

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