

Abb. 6. Trennung II: Die Verteilung von Li-6 längs des Troges nach 12,7 Tagen (gestrichelt) und 32,8 Tagen (ausgezogene Kurve). Trennfaktor 5,9 bzw. 12,8.  
Abszisse: Nummer der Trogkammer.

Die Abb. 5 und 6 schließlich zeigen den Verlauf des Molenbruchs von Li-6 längs des Troges, und zwar bei Trennung I nach 9 Betriebstagen, bei Trennung II nach 12,7 und 32,8 Tagen. Offensichtlich ist nach 32,8 Tagen die Endtrennung praktisch erreicht. Man findet als Trennfaktor zwischen den jeweils äußersten Meßpunkten der Abb. 5 bzw. 6:

$$Q_I = 3,1 \text{ (9 Tage)},$$

$$Q_{II} = 5,9 \text{ (12,7 Tage) bzw. } 12,8 \text{ (32,8 Tage)}.$$

Nimmt man für den Beweglichkeitsunterschied der isotonen Ionen  $^6\text{Li}^+$  und  $^7\text{Li}^+$  einen mittleren Wert von rund 0,08% an, dann läßt sich auf Grund der beobachteten Trennfaktoren die unter den jeweiligen Betriebsdaten erreichte Bodenzahl angeben:

$$n_{BII} = 3180 \text{ (32,8 Tage)}.$$

$$n_{BI} = 1440 \text{ (9 Tage)},$$

## Nitrogen Isotope Exchange between Liquid $\text{N}_2\text{O}_3$ and NO at Low Temperature and Elevated Pressure\*

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The single stage separation factor,  $\alpha$ , for nitrogen isotope exchange between liquid  $\text{N}_2\text{O}_3$ — $\text{N}_2\text{O}_4$  mixtures and their vapor has been measured at temperatures ranging from  $-76^\circ\text{C}$  to room temperature and pressures between 1 atm. and 7.4 atm.

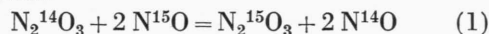
|                                      |                              |
|--------------------------------------|------------------------------|
| At $-76^\circ\text{C}$ and 1 atm.,   | $\alpha = 1.061 \pm 0.003$ ; |
| at $-23^\circ\text{C}$ and 1 atm.,   | $\alpha = 1.034 \pm 0.002$ ; |
| at $+23^\circ\text{C}$ and 2.1 atm., | $\alpha = 1.017 \pm 0.002$ ; |
| at $+23^\circ\text{C}$ and 7.4 atm., | $\alpha = 1.030 \pm 0.002$ . |

The results are compared with values, calculated from spectroscopic data for  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$ , NO and  $\text{NO}_2$ . The value of  $\alpha = 1.030$  found at room temperature and 7.4 atm. pressure enhances the usefulness of the  $\text{N}_2\text{O}_3$ —NO-system for separating the nitrogen isotopes, since it eliminates the need of refrigeration.

In recent years several new processes for concentrating nitrogen-15 have been explored and developed, motivated at least partly by the low neutron absorption cross-section of this isotope and the possibility of a large scale application in nuclear reactors. The most promising systems for a large scale con-

centration include exchange between nitric acid and nitric oxide<sup>1</sup>, distillation of liquid nitric oxide<sup>2</sup>, and exchange between liquid  $\text{N}_2\text{O}_3$  and nitric oxide<sup>3</sup>.

The latter system, which may be represented by the equation



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<sup>1</sup> W. SPINDEL and T. I. TAYLOR, J. Chem. Phys. **24**, 626 [1956]; Trans. N.Y. Acad. Sci. **19**, 3 [1956]. — T. I. TAYLOR and W. SPINDEL, Proc. Int. Symposium of Isotope Separation, North-Holland Publ. Comp., Amsterdam 1958, p. 158.

<sup>2</sup> K. CLUSIUS and K. SCHLEICH, Helv. Chim. Acta **41**, 1342 [1958]. — K. CLUSIUS, M. VECCHI, A. FISCHER and U. PIES-

BERGEN, Helv. Chim. Acta **42**, 1975 [1959]. — K. CLUSIUS, K. SCHLEICH and M. VECCHI, Helv. Chim. Acta **42**, 2654 [1959]. — K. CLUSIUS and K. SCHLEICH, Helv. Chim. Acta **42**, 232 [1959]. — K. CLUSIUS and M. VECCHI, Helv. Chim. Acta **42**, 1921 [1959]. — K. CLUSIUS, K. SCHLEICH and M. VECCHI, Helv. Chim. Acta **44**, 343 [1961].

<sup>3</sup> E. U. MONSE, W. SPINDEL, LOIS NASH KAUDER and T. I. TAYLOR, J. Chem. Phys. **32**, 1557 [1960].

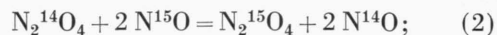


appears promising because of the fairly large single stage factor,  $\alpha$ , which ranges from 1.035 at  $-14^\circ\text{C}$  to 1.016 at  $+14^\circ\text{C}$ , and because of the rapidity of the exchange. A small laboratory cascade consisting of two exchange columns of 2.5 and 3.0 m in length, operated at  $-9^\circ\text{C}$  and 1 atm. pressure proved sufficient to prepare 99.7% nitrogen-15 at rates between 0.3 and 0.5 g  $\text{N}^{15}$  per day<sup>4</sup>.

A comparison of the present system with the  $\text{NO}-\text{HNO}_3$  exchange system<sup>1</sup>, which is used for commercial preparation of  $\text{N}^{15}$ , indicated that approximately equal volumes of column would be required for the same separation task in spite of a considerably lower  $\alpha$  for the  $\text{N}_2\text{O}_3-\text{NO}$  system. A disadvantage of the  $\text{N}_2\text{O}_3-\text{NO}$  system, in contrast to the  $\text{HNO}_3-\text{NO}$  system, which can be operated conveniently at ambient temperature, is the necessity for refrigeration. Obviously, the usefulness of the  $\text{N}_2\text{O}_3-\text{NO}$  system would be improved, if it could be operated at room temperature without decreasing the separation factor. Preliminary calculations indicated that this might be achieved by increasing the pressure of the system above atmospheric<sup>5</sup>. As an additional advantage, operation at higher pressure should reduce the effective stage height for a given throughput of material.

The sensitivity of the single stage factor,  $\alpha$ , towards changes in pressure and temperature is due to changes in the chemical composition of the system. The system has been described as involving the isotope exchange between  $\text{N}_2\text{O}_3$  in the liquid and  $\text{NO}$  in the gas. However, at a temperature in the order of  $0^\circ\text{C}$  and at atmospheric pressure, a number of other chemical components are formed in appreciable quantities. The liquid contains  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$  and  $\text{NO}$ ; the gas phase contains  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$ ,  $\text{NO}_2$  and  $\text{NO}$ <sup>6-9</sup>. Isotope exchange occurs among all of these species. The effective single stage factor,  $\alpha$ , is determined by three independent exchange reactions<sup>3</sup> if fractionation due to isotope effects in condensed phases is neglected. The controlling reactions are: the exchange between  $\text{N}_2\text{O}_3$  and  $\text{NO}$ ,

according to equation (1); the exchange between  $\text{N}_2\text{O}_4$  and  $\text{NO}$  according to



and the exchange between  $\text{NO}_2$  and  $\text{NO}$  according to



Nitrogen-15 is enriched in all those species containing nitrogen in the  $+4$  oxidation state, since there are additional bonds to  $+4$  nitrogen.

Raising the pressure or lowering the temperature reduces the ratio of  $+4$  to  $+2$  in the gas phase relative to the same ratio in the liquid, and therefore increases the N-isotope fractionation,  $\alpha$ , between the two phases. At temperatures below  $-10^\circ\text{C}$ , where the gas phase already consists mainly of  $+2$  nitrogen ( $\text{NO}$ ) at atmospheric pressure, an increase of pressure has little effect on the composition and therefore on the single stage factor,  $\alpha$ . However, at a temperature of about  $20^\circ\text{C}$ , appreciable amounts of  $+4$  nitrogen are present in the gas at atmospheric pressure, and increasing the pressure can yield an appreciable increase in the separation factor,  $\alpha$ .

At high pressures or at low temperatures, the system consists primarily of  $\text{N}_2\text{O}_3$  in the liquid and  $\text{NO}$  in the gas, and the isotope exchange is dominated by reaction (1). The isotope fractionation factor,  $\alpha$ , measured under these conditions approaches the square root of the equilibrium constant for exchange reaction (1).

In order to study the pressure and temperature dependence of the single stage factor,  $\alpha$ , for the  $\text{N}_2\text{O}_3-\text{NO}$  exchange, measurements of  $\alpha$  were carried out at  $-76^\circ\text{C}$  and atmospheric pressure, at  $-23^\circ\text{C}$  and atmospheric pressure, and also at room temperature and elevated pressures. The results are compared with values calculated from spectroscopic data for  $\text{N}_2\text{O}_3$ <sup>10</sup>,  $\text{N}_2\text{O}_4$ <sup>11</sup>,  $\text{NO}_2$ <sup>12</sup> and  $\text{NO}$ <sup>13</sup>.

<sup>4</sup> E. U. MONSE, T. I. TAYLOR and W. SPINDEL, *J. Phys. Chem.* **65**, 1625 [1961].

<sup>5</sup> E. U. MONSE, *J. Chem. Phys.* **33**, 312 [1960].

<sup>6</sup> G. BAUME and M. ROBERT, *C. R. Acad. Sci., Paris* **169**, 970 [1919].

<sup>7</sup> R. H. PURCELL and G. H. CHEESMAN, *J. Chem. Soc.* **1932**, 834.

<sup>8</sup> I. R. BEATTIE and A. J. VOSPER, *J. Chem. Soc.* **1960**, 4799.

<sup>9</sup> I. R. BEATTIE and A. J. VOSPER, *J. Chem. Soc.* **1961**, 2106.

<sup>10</sup> I. C. HISATSUNE and J. P. DEVLIN, *Spectrochim. Acta* **16**, 401 [1960]. — J. P. DEVLIN and I. C. HISATSUNE, *Spectrochim. Acta* **17**, 218 [1961].

<sup>11</sup> I. C. HISATSUNE, J. P. DEVLIN and Y. WADA, *J. Chem. Phys.* **33**, 714 [1960]. — G. M. BEGUN and W. H. FLETCHER, *J. Mol. Spectroscopy* **4**, 388 [1960].

<sup>12</sup> E. T. ARAKAWA and A. H. NIELSEN, *J. Mol. Spectroscopy* **2**, 413 [1958].

<sup>13</sup> R. H. GILLETTE and E. H. EYSTER, *Phys. Rev.* **56**, 1113 [1939].

### Chemical Composition of Mixtures of NO and $\text{NO}_2$

As pointed out earlier, isotope exchange between liquid and gaseous NO- $\text{NO}_2$  mixtures involves several exchange reactions, and the effective separation factor is determined by the quantities of all the exchangeable species present in each phase. A complete knowledge of the chemical composition of the system is required to correlate the fractionation factors of the individual exchange reactions (1) to (3) with the total isotope fractionation between the two phases.

Two-phase equilibria of NO- $\text{NO}_2$  mixtures have been studied by several authors<sup>6-9</sup>. They found that the amount of +4 nitrogen in each phase is determined by fixing the pressure and temperature. In other words, an NO- $\text{NO}_2$  mixture with a given +4 nitrogen content exerts a certain vapor pressure depending on the temperature of the mixture. BEATTIE and VOSPER<sup>8</sup> have recently measured the vapor pressure of NO- $\text{NO}_2$  mixtures between  $-60^\circ\text{C}$  and  $+20^\circ\text{C}$  and express their results by the empirical formula:

$$\log_{10}(\text{pressure in mm}) = 8.95 - f(X)/T, \quad (4)$$

where  $f(X)$  is a function of the mole fraction,  $X$ , of +4 nitrogen in the liquid, and  $T$  is the absolute temperature. The same authors have concluded that the vapor composition (i. e. the ratio of +4 nitrogen to +2 nitrogen) above liquid NO- $\text{NO}_2$  mixtures depends only on the composition of the liquid phase at any temperature and pressure. Further, their results indicate that liquid NO- $\text{NO}_2$  mixtures consist mainly of  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$  with almost no physically dissolved NO.

The composition of the gas phase in terms of all the species NO,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$  can be obtained from the mole fraction of +4 nitrogen,  $x$ , for a given temperature and pressure. It is related to the partial pressures of  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$ , NO and  $\text{NO}_2$  ( $p_1$ ,  $p_2$ ,  $p_3$ ,  $p_4$ ); the total pressure,  $p$ , and the dissociation constants of  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$  ( $K_1$  and  $K_2$ ), by the set of equations:

$$p = p_1 + p_2 + p_3 + p_4, \quad (5)$$

$$x = \frac{p_1 + 2p_2 + p_4}{2p_1 + 2p_2 + p_3 + p_4}, \quad (6)$$

$$p_1 = K_1 p_3 p_4, \quad p_4^2 = K_2 p_2. \quad (7), (8)$$

Here,  $p$ ,  $x$ ,  $K_1$  and  $K_2$  are known for a given value of  $X$ , in the liquid phase, and a given temperature. The equations can therefore be solved for the unknown partial pressures,  $p_i$ .

Actually, the dissociation constants  $K_1$  and  $K_2$  for  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$  are slightly dependent upon the pressure, because of the non-ideal character of the gases<sup>14-16</sup>, but this pressure dependence may be neglected for the present calculations. Over the experimental pressure range, an average value for  $K_1$  was used, extrapolated from the results reported by ABEL and PROISL<sup>14</sup> and BEATTIE and BELL<sup>15</sup>. The value of  $K_2$  used was that of WOURTZEL<sup>17</sup>.

With the help of equations (4) - (8) and a relationship between the +4 nitrogen content,  $X$ , and  $x$ , in the two phases, as given by BEATTIE and VOSPER<sup>9</sup>, the concentrations of all chemical species in each phase can be determined within the temperature and pressure range for which the relationships apply, i. e. approximately from  $-60^\circ\text{C}$  to room temperature, and pressures below 1 atm. Since the present investigation involved vapor pressures of liquid NO- $\text{NO}_2$  mixtures above 1 atmosphere, the validity of the relationships was tested for higher pressures.

### Experimental Method

The vapor pressure measurements of NO- $\text{NO}_2$  mixtures were carried out in a stainless steel vessel of about 80 cc volume, equipped with a stainless steel bourdon-type gauge. Known amounts of NO and  $\text{NO}_2$  were mixed in a five liter bulb and then frozen with liquid nitrogen into the pressure vessel. The vessel was then warmed and surrounded by a constant temperature bath at  $26^\circ\text{C}$  for the reading of the pressure. The composition of the liquid is related to the original amounts,  $n_1$  and  $n_2$  (in mg. atoms nitrogen) of NO and  $\text{NO}_2$ , respectively by:

$$X = (n_2 - a'x)/(n_1 + n_2 - a'). \quad (9)$$

Here  $X$ , and  $x$ , have the same meaning as previously and  $a'$  is the total number of mg atoms nitrogen in the gas phase.

The gas phase was analyzed for its +4 nitrogen content by transferring a gas sample ( $\sim 80-100$  cc. atm.) from the highpressure stainless steel vessel, into a calibrated glass vessel (about 250 cc.), which was maintained at liquid nitrogen temperature. Then a known amount of oxygen was introduced, to oxidize the NO. The pressure of  $\text{NO}_2$  plus the excess oxygen was measured at room temperature, using a mercury

<sup>14</sup> E. ABEL and J. PROISL, Z. Elektrochem. **35**, 712 [1929].

<sup>15</sup> E. R. BEATTIE and S. W. BELL, J. Chem. Soc. **1957**, 1681.

<sup>16</sup> F. H. VERHOEK and F. DANIELS, J. Amer. Chem. Soc. **53**, 1250 [1931].

<sup>17</sup> E. WOURTZEL, C. R. Acad. Sci., Paris **169**, 1397 [1919].

manometer; the mercury was protected by a layer of  $\alpha$ -bromonaphthalene. Finally after pumping off the excess oxygen, while holding back the  $\text{NO}_2$  at liquid nitrogen temperature, the pressure of the  $\text{NO}_2$  alone was determined at room temperature.

From the pressure measurements described above, the total amount of nitrogen in the gas sample and the net amount of oxygen required to oxidize the +2 nitrogen can be determined. Thus, the mole fraction of +2 and +4 nitrogen in each gas sample is found.

### Results

The results of vapor pressure measurements between about 3 and 9.5 atm. as a function of the mole fraction,  $X$ , of the +4 nitrogen in the liquid phase at 26 °C, are shown in Fig. 1. The results agree within the experimental error (for  $X$ :  $\pm .005$ ; for  $p$ :  $\pm .05$  atm.) with the work of BEATTIE and VOSPER<sup>8</sup>, but there is poor agreement with extrapolated values taken from an earlier investigation by BAUME and ROBERT<sup>6</sup>.

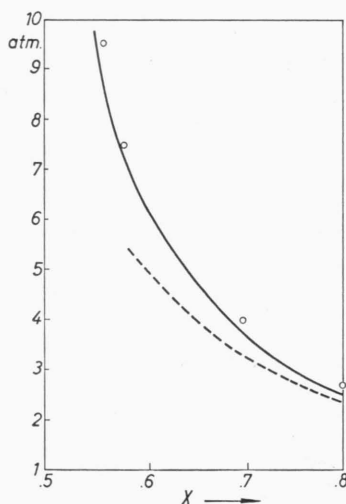


Fig. 1. Vapor pressure of  $\text{NO}-\text{NO}_2$  mixtures as a Function of the Mole fraction,  $X$ , of +4 Nitrogen at 26 °C (liquid).  $\circ$  = Experimental Points, this paper; — = Extrapolated Values, ref. <sup>8</sup>; ---- = Extrapolated Values, ref. <sup>6</sup>.

The results of the gas analysis are presented in Fig. 2, where the mole fraction,  $x$ , of +4 nitrogen in the gas phase is plotted against the mole fraction,  $X$ , of +4 nitrogen in the liquid. Again, within the experimental error (for  $x$ :  $\pm .05$ ), the agreement with BEATTIE and VOSPER's results<sup>9</sup> and those of PURCELL and CHEESMAN<sup>7</sup> is satisfactory.

Thus, from our results it can be concluded that an extrapolation to higher vapor pressures of

$\text{NO}-\text{NO}_2$  mixtures at room temperature according to equation (4) is justified.

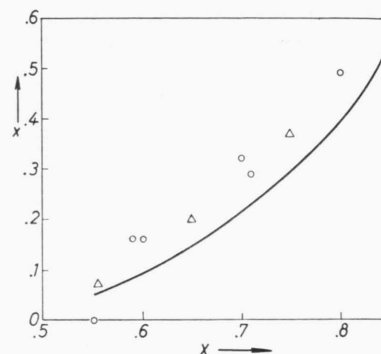


Fig. 2. Mole fraction,  $x$ , of +4 Nitrogen in the gas as a function of the Mole fraction,  $X$ , of +4 Nitrogen in the liquid.  $\circ$  = Experimental Points, this paper;  $\triangle$  = Experimental Points, ref. <sup>7</sup>; — = Extrapolated Values, ref. <sup>9</sup>.

Further, from our gas analysis, in conjunction with earlier results<sup>9</sup>, it follows that the composition of the gas phase depends only on the liquid phase composition for any temperature and pressure.

### Effective Isotope Fractionation Factor

The nitrogen isotope exchange between liquid  $\text{NO}-\text{NO}_2$  mixtures and the vapor phase above these mixtures, was studied at  $-76$  °C and 1 atm. pressure, at  $-23$  °C and 1 atm. pressure, and at room temperature and pressures ranging from 2 to 9.5 atmospheres.

### Experimental Method

The equilibrations at  $-76$  °C were carried out in a glass vessel of  $\sim 180$  cc volume. Equivalent amounts of  $\text{NO}$  and  $\text{NO}_2$  were transferred into the vessel, which was maintained at operating temperature with a bath of dry ice-trichlorethylene slush. More  $\text{NO}$  was added until the gas phase reached a pressure of 1 atm. The liquid  $\text{N}_2\text{O}_3$  was stirred for periods of 1 to 12 days, after which time gas samples were withdrawn for isotope analysis. Finally, the liquid and remaining gas were evaporated into a large bulb, from which samples were taken to determine the isotopic composition of the combined phases.

For the equilibrations at  $-23$  °C, a jacketed reaction vessel (150 cc volume) was used, and temperature control was achieved by circulating a refrigerated coolant.

The equilibrations at elevated pressures were carried out in the stainless steel vessel described above. Known amounts,  $n_1$  and  $n_2$ , of  $\text{NO}$  and  $\text{NO}_2$  were frozen into



the vessel with liquid nitrogen, so as to yield the desired pressure. The vessel was warmed to room temperature and shaken for periods of 1–4 days to ensure attainment of isotopic equilibrium. The sampling procedure for isotope analysis was the same as for the low temperature experiments. All isotope samples were reduced to elemental nitrogen at 750 °C in a fused silica tube, filled with a mixture of copper and copper oxide. The isotope ratios were measured in a Consolidated-Nier mass spectrometer, Model 21-201.

### Results

The results of the equilibrations at  $-76^{\circ}$ ,  $-23^{\circ}$  and  $23^{\circ}$  C are shown in Tables 1, 2, and 3. The isotope fractionation factor,  $\alpha$ , defined as the quotient of the N<sup>15</sup>/N<sup>14</sup> ratio in the liquid and in the gas was calculated by

$$\alpha = \frac{R_{\text{liq} + \text{gas}}}{R_{\text{gas}}} + \frac{a}{A} \left[ \frac{R_{\text{liq} + \text{gas}}}{R_{\text{gas}}} - 1 \right] \quad (10)$$

where  $R_{\text{gas}}$  and  $R_{\text{liq} + \text{gas}}$  are the N<sup>15</sup>/N<sup>14</sup> ratios in the gas and combined liquid and gas phases, respectively, and  $a$  and  $A$  are the number of g-atoms N in the gas and liquid. The scatter of the results,  $\pm .002$  to  $\pm .003$ , is in the same order as the mass spectrometric error,  $\pm .002$ .

| Run No. | Equilibration time, days | $a/A$<br>g atom N (gas)<br>g atom N (liq) | $\frac{R_{\text{liq} + \text{gas}}}{R_{\text{gas}}}$ | $\alpha$ |
|---------|--------------------------|---|--|----------|
| 2       | 3                        | 0.07                                      | 1.055  | 1.059    |
| 3       | 4                        | 0.07                                      | 1.059  | 1.063    |
| 6       | 4                        | 0.07                                      | 1.055  | 1.059    |
| 7       | 4                        | 0.07                                      | 1.059  | 1.063    |
| 8       | 12                       | 0.07                                      | 1.058  | 1.062    |
| 9       | 4                        | 0.14                                      | 1.051  | 1.058    |
| 10      | 2                        | 0.14                                      | 1.053  | 1.060    |

Table 1. Single stage separation factor,  $\alpha$ , at  $-76^{\circ}$  C and 1 atm. pressure.

| Run No. | Equilibration time, days | $a/A$<br>g atom N (gas)<br>g atom N (liq) | $\frac{R_{\text{liq} + \text{gas}}}{R_{\text{gas}}}$ | $\alpha$ |
|---------|--------------------------|---|--|----------|
| 29      | 2                        | 0.05                                      | 1.032  | 1.034    |
| 30      | 1                        | 0.05                                      | 1.030  | 1.032    |
| 31      | 1                        | 0.05                                      | 1.033  | 1.035    |

Table 2. Single stage separation factor,  $\alpha$ , at  $-23^{\circ}$  C and 1 atm. pressure.

| Run No. | pressure atm. | Equilibration time, days | $a/A$<br>g atoms N (gas)<br>g atoms N (liq) | $\frac{R_{\text{liq} + \text{gas}}}{R_{\text{gas}}}$ | $\alpha$ |
|---------|---------------|--------------------------|---|--|----------|
| 20      | 2.1           | 1                        | 0.08  | 1.016  | 1.017    |
| 21      | 2.1           | 4                        | 0.08  | 1.017  | 1.018    |
| 18      | 3.2           | 5                        | 0.13  | 1.022  | 1.025    |
| 19      | 3.2           | 1                        | 0.13  | 1.022  | 1.025    |
| 22      | 3.2           | 2                        | 0.15  | 1.018  | 1.021    |
| 4       | 4.0           | 4                        | 0.07  | 1.025  | 1.027    |
| 5       | 4.0           | 1                        | 0.07  | 1.026  | 1.028    |
| 11      | 5.0           | 1                        | 0.12  | 1.024  | 1.027    |
| 12      | 5.0           | 4                        | 0.12  | 1.022  | 1.025    |
| 13      | 5.0           | 1                        | 0.12  | 1.025  | 1.028    |
| 14      | 5.0           | 1                        | 0.13  | 1.026  | 1.029    |
| 17      | 5.0           | 4                        | 0.13  | 1.022  | 1.025    |
| 15      | 7.4           | 4                        | 0.18  | 1.025  | 1.030    |
| 16      | 7.4           | 1                        | 0.18  | 1.025  | 1.030    |

Table 3. Single stage separation factor,  $\alpha$ , at  $+23^{\circ}$  C and elevated pressures.

### Discussion and Summary

The results of the equilibrations may be compared with values for the fractionation factor,  $\alpha$ , calculated from spectroscopic data. In a manner similar to that shown previously<sup>3</sup>,  $\alpha$  becomes a weighted average of the equilibrium constants  $K_{13}$ ,  $K_{23}$ , and  $K_{43}$  of the exchange reactions (1), (2), and (3), respectively:

$$\alpha = \frac{M_1 K_{13}^{1/2} + M_2 K_{23}^{1/2} + M_3}{m_1 K_{13}^{1/2} + m_2 K_{23}^{1/2} + m_3 + m_4 K_{43}} \quad (11)$$

Here  $M_1$ ,  $M_2$ ,  $M_3$ ,  $m_1$ ,  $m_2$ ,  $m_3$  and  $m_4$  are the mole fractions of nitrogen as N<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O<sub>4</sub>, NO and NO<sub>2</sub> in the liquid and gas phase respectively. The values of  $K_{13}^{1/2}$ ,  $K_{23}^{1/2}$  and  $K_{43}$  for various temperatures were calculated from spectroscopic data<sup>18</sup> of N<sub>2</sub>O<sub>3</sub><sup>10</sup>, N<sub>2</sub>O<sub>4</sub><sup>11</sup>, NO<sub>2</sub><sup>12</sup> and NO<sup>13</sup> according to the method of BIGEISEN and MAYER<sup>19</sup> and are listed in Table 4. The values in the upper section of Table 4 refer to  $(1/n) \ln f$ , where  $n$  is the number of exchangeable nitrogen atoms and  $f$  is the partition function ratio of the fully isotopically substituted molecules<sup>19</sup>.

The substitution of  $K_{13}^{1/2}$  in equation (11) is not strictly correct, since the nitrogen atoms in the asymmetric molecule N<sub>2</sub>O<sub>3</sub> occupy nonequivalent

<sup>18</sup> Two bands were observed by HISATSUNE and DELIN<sup>10</sup> for the symmetric nitro bond stretching frequency  $\nu_3$  of N<sup>15</sup>O<sub>3</sub>, namely at 1277 and 1297 cm<sup>-1</sup>. For the calculation of  $K_{13}^{1/2}$  the arithmetic mean,  $\nu_3 = 1287$  cm<sup>-1</sup> was used.

<sup>19</sup> J. BIGEISEN and M. GÖPPERT-MAYER, J. Chem. Phys. **15**, 261 [1947].

|                                | N <sub>2</sub> O <sub>4</sub>  | N <sub>2</sub> O <sub>3</sub> | NO <sub>2</sub> | NO    | Temp.<br>°K |
|--------------------------------|--------------------------------|-------------------------------|-----------------|-------|-------------|
| 1/n ln f                       | .2340                          | .1753                         | .1857           | .1062 | 193.1       |
|                                | .1775                          | .1290                         | .1382           | .0819 | 243.1       |
|                                | .1546                          | .1157                         | .1244           | .0757 | 263.1       |
|                                | .1468                          | .1099                         | .1183           | .0723 | 273.1       |
|                                | .1395                          | .1042                         | .1126           | .0690 | 283.1       |
|                                | .1328                          | .0995                         | .1074           | .0661 | 293.1       |
|                                | .0930                          | .0698                         | .0759           | .0481 | 373.1       |
|                                |                                |                               |                 |       |             |
| K <sub>13</sub> <sup>1/2</sup> | K <sub>23</sub> <sup>1/2</sup> | K <sub>43</sub>               | Temp. °K        |       |             |
| 1.072                          | 1.136                          | 1.083                         | 193.1           |       |             |
| 1.048                          | 1.100                          | 1.058                         | 243.1           |       |             |
| 1.041                          | 1.082                          | 1.050                         | 263.1           |       |             |
| 1.038                          | 1.078                          | 1.047                         | 273.1           |       |             |
| 1.036                          | 1.073                          | 1.045                         | 283.1           |       |             |
| 1.034                          | 1.069                          | 1.042                         | 293.1           |       |             |
| 1.022                          | 1.046                          | 1.028                         | 373.1           |       |             |

Table 4. Equilibrium constants for nitrogen exchange.

positions<sup>10</sup>. However, due to rapid exchange between N<sub>2</sub>O<sub>3</sub>, NO<sub>2</sub> and NO, the four isotopic molecules ON<sup>14</sup>N<sup>14</sup>O<sub>2</sub>, ON<sup>14</sup>N<sup>15</sup>O<sub>2</sub>, ON<sup>15</sup>N<sup>14</sup>O<sub>2</sub> and ON<sup>15</sup>N<sup>15</sup>O<sub>2</sub> are in equilibrium with each other. Practically no distinction between ON<sup>14</sup>N<sup>15</sup>O<sub>2</sub> and ON<sup>15</sup>N<sup>14</sup>O<sub>2</sub> is possible. It seems therefore justified to assume for the isotopic N<sub>2</sub>O<sub>3</sub>-molecules a statistical distribution similar to that for symmetric N<sub>2</sub>O<sub>4</sub>.

The mole fractions  $m_i$  in the gas phase were calculated using equations (5) to (8). Since dissociation of N<sub>2</sub>O<sub>3</sub> in the liquid cannot be excluded, the liquid was assumed to consist either of N<sub>2</sub>O<sub>3</sub> and N<sub>2</sub>O<sub>4</sub> ( $M_3=0$ ) or of N<sub>2</sub>O<sub>4</sub> and NO ( $M_1'=0$ ).

The results of the calculations are summarized in Tables 5 and 6. The fractionation factor,  $\alpha$ , is shown as a function of temperature for the NO—NO<sub>2</sub> system at 1 atm. pressure and as a function of pressure at 23 °C respectively.

The values for  $\alpha$  in Tables 5 and 6 are plotted in Figs. 3 and 4 and compared with the experimental results. The solid curve in these graphs represents calculated  $\alpha$  values, assuming a liquid composition of N<sub>2</sub>O<sub>3</sub> and N<sub>2</sub>O<sub>4</sub>. The dashed line refers to a hypothetical liquid composition of N<sub>2</sub>O<sub>4</sub> and NO. The circles represent the experimental results with the error indicated by extensions on these points. The experimental values, at -9 °C and -14 °C in Fig. 3 were taken from earlier work on the N<sub>2</sub>O<sub>3</sub>—NO exchange<sup>3</sup>.

The agreement between the observed and calculated value of the fractionation factor,  $\alpha$ , is satisfactory, if one takes into account both the experimental error and the uncertainty of calculated values. This uncertainty arises from the limited accuracy of the spectroscopic data used, and the neglect of interactions in the condensed state.

It may be noted, that the calculated values of  $\alpha$  are nearly independent of the hypothetical composition of the liquid. This result is fortuitous and stems from the numerical value of the equilibrium constants  $K_{13}$  and  $K_{23}$ . The calculations, based on spectroscopic data, show that for all temperatures,  $K_{13}^{1/2} - 1 \cong \frac{1}{2} (K_{23}^{1/2} - 1)$ . This leads for any mole fraction of +4 nitrogen,  $X$ , to approximately the same  $\alpha$  for both hypothetical compositions of the

| Temp.<br>°K |                | X              | x              | Partial pressure (atm.) |                |                |       |                  |                  |                |  |
|-------------|----------------|----------------|----------------|-------------------------|----------------|----------------|-------|------------------|------------------|----------------|--|
|             |                |                |                | p <sub>1</sub>          |                | p <sub>2</sub> |       | p <sub>3</sub>   |                  | p <sub>4</sub> |  |
| 193.1       |                | 0.50           | 0.00           | 0.000                   |                | 0.000          |       | 1.000            |                  | 0.000          |  |
| 243.1       |                | 0.52           | 0.04           | 0.037                   |                | 0.002          |       | 0.960            |                  | 0.001          |  |
| 263.1       |                | 0.62           | 0.09           | 0.055                   |                | 0.015          |       | 0.920            |                  | 0.010          |  |
| 283.1       |                | 0.84           | 0.50           | 0.090                   |                | 0.236          |       | 0.573            |                  | 0.101          |  |
| 293.1       |                | 1.00           | 1.00           | 0.000                   |                | 0.733          |       | 0.000            |                  | 0.267          |  |
|             |                |                |                |                         |                |                |       |                  |                  |                |  |
| Temp.°K     | m <sub>1</sub> | m <sub>2</sub> | m <sub>3</sub> | m <sub>4</sub>          | M <sub>1</sub> | M <sub>2</sub> | α     | M <sub>2</sub> ' | M <sub>3</sub> ' | α'             |  |
| 193.1       | 0.000          | 0.000          | 1.000          | 0.000                   | 1.00           | 0.00           | 1.072 | 0.50             | 0.50             | 1.068          |  |
| 243.1       | 0.071          | 0.004          | 0.924          | 0.001                   | 0.96           | 0.04           | 1.046 | 0.52             | 0.48             | 1.048          |  |
| 263.1       | 0.103          | 0.028          | 0.860          | 0.009                   | 0.76           | 0.24           | 1.043 | 0.62             | 0.38             | 1.044          |  |
| 283.1       | 0.136          | 0.356          | 0.432          | 0.076                   | 0.32           | 0.68           | 1.026 | 0.84             | 0.16             | 1.026          |  |
| 293.1       | 0.000          | 0.846          | 0.000          | 0.154                   | 0.00           | 1.00           | 1.004 | 1.00             | 0.00             | 1.004          |  |

Table 5. Single stage separation factor,  $\alpha$ , between -80 °C and +20 °C, at 1 atm. pressure [calculated via equ. (11) using the values of  $K_{13}^{1/2}$ ,  $K_{23}^{1/2}$  and  $K_{43}$  in Table 4].

| $p$<br>atm | $X$  | $x$  | partial pressure (atm.) |       |       |       | $\alpha$ | $M'_2$ | $M'_3$ | $\alpha'$ |
|------------|------|------|-------------------------|-------|-------|-------|----------|--------|--------|-----------|
|            |      |      | $p_1$                   | $p_2$ | $p_3$ | $p_4$ |          |        |        |           |
| 2          | 0.83 | 0.50 | 0.197                   | 0.445 | 1.124 | 0.234 |          |        |        |           |
| 3          | 0.72 | 0.24 | 0.269                   | 0.203 | 2.370 | 0.158 |          |        |        |           |
| 5          | 0.61 | 0.08 | 0.254                   | 0.047 | 4.623 | 0.076 |          |        |        |           |
| 7          | 0.55 | 0.04 | 0.213                   | 0.016 | 6.727 | 0.044 |          |        |        |           |
| 10         | 0.52 | 0.03 | 0.251                   | 0.011 | 9.702 | 0.036 |          |        |        |           |

| $p$ atm | $m_1$ | $m_2$ | $m_3$ | $m_4$ | $M_1$ | $M_2$ | $\alpha$ | $M'_2$ | $M'_3$ | $\alpha'$ |
|---------|-------|-------|-------|-------|-------|-------|----------|--------|--------|-----------|
| 2       | 0.149 | 0.337 | 0.425 | 0.089 | 0.34  | 0.66  | 1.024    | 0.83   | 0.17   | 1.024     |
| 3       | 0.155 | 0.117 | 0.682 | 0.046 | 0.56  | 0.44  | 1.033    | 0.72   | 0.28   | 1.033     |
| 5       | 0.096 | 0.018 | 0.872 | 0.014 | 0.78  | 0.22  | 1.036    | 0.61   | 0.39   | 1.036     |
| 7       | 0.059 | 0.004 | 0.931 | 0.006 | 0.90  | 0.10  | 1.035    | 0.55   | 0.45   | 1.035     |
| 10      | 0.049 | 0.002 | 0.945 | 0.004 | 0.96  | 0.04  | 1.033    | 0.52   | 0.48   | 1.033     |

Table 6. Single stage separation factor,  $\alpha$ , at +23 °C and elevated pressures [calculated via equ. (11);  $K_{13}^{1/2}=1.034$ ;  $K_{23}^{1/2}=1.068$ ;  $K_{43}=1.041$ ].

liquid. Consequently a comparison between calculated and observed values gives no indication about the true composition of the liquid.

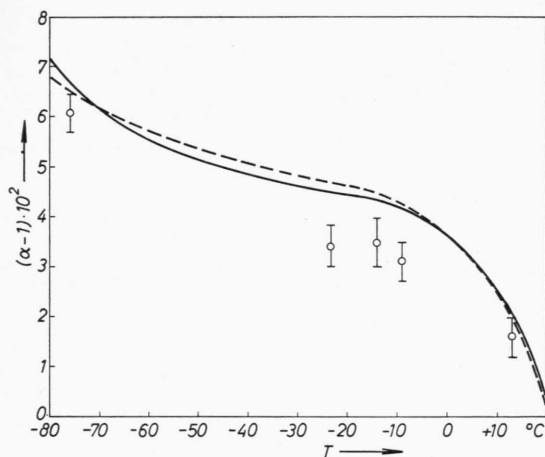


Fig. 3. Effective Single Stage Separation Factor,  $\alpha$ , between -80° and +20 °C at 1 atm.

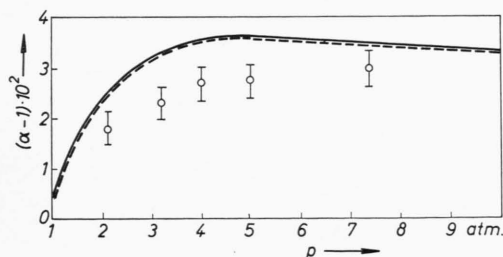


Fig. 4. Effective Single Stage Separation Factor,  $\alpha$ , at 23 °C between 1 and 10 atm.

The shapes of the curves, Figs. 3 and 4, characterize the main features of the factor,  $\alpha$ , with regard to its temperature and pressure dependence. Lowering the temperature to about -10 °C at atmospheric pressure has almost the same effect on  $\alpha$  as increasing the pressure to about 4 atm. at room temperature. As expected, the single stage factor,  $\alpha$ , rises with increasing pressure, or decreasing temperature, until the point is reached where the liquid consists essentially of N<sub>2</sub>O<sub>3</sub> in equilibrium with almost pure NO in the gas. This point is the inflection point in Fig. 3, which occurs at about -30 °C. From there on the single stage factor,  $\alpha$ , becomes equal to  $K_{13}$  and rises according to the quantum statistical temperature dependence of  $K_{13}$ . At room temperature, the "pure" N<sub>2</sub>O<sub>3</sub>-NO system is approached with increasing pressure, where the single stage factor,  $\alpha$ , becomes almost insensitive to changes in pressure.

The high value of  $\alpha = 1.030$ , found at 23 °C and a pressure of about 7 atm. enhances the usefulness of the N<sub>2</sub>O<sub>3</sub>-NO system for separating the nitrogen isotopes, since it eliminates the need for refrigeration. In addition, it can be hoped that the higher temperature would decrease the stage height of exchange columns, and that high pressure operation would permit a larger throughput of material.

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