319. *Dinitrogen Trioxide. Part I. Stability in the Gaseous Phase.*

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By use of an all-glass apparatus the equilibrium between nitrogen dioxide, dinitrogen tetroxide, nitric oxide, and dinitrogen trioxide has been studied in the gas phase at 5°, 15°, 25°, 35°, and 45°. The equilibrium constant at each temperature has been determined over a wide concentration range, enabling thermodynamic constants to be obtained by extrapolation to zero pressure. Values of $\Delta S°$ and $\Delta H°$ are given.

ALTHOUGH the existence of dinitrogen trioxide has long been assumed very little is known of its properties. It is nevertheless of considerable interest. It has been suggested that it is the active species in *N*-nitrosation and an anticatalyst in nitrations involving the nitronium ion.[1] It is also important in the formation of certain complexes,[2] while the majority of systems containing oxides of nitrogen contain amounts of dinitrogen trioxide

¹ See, *e.g.*, Ingold, " Structure and Mechanism in Organic Chemistry," Bell & Sons Ltd., London, 1953, pp. 284, 398.
² Pearson, Henry, Bergmann, and Basolo, *J. Amer. Chem. Soc.*, 1954, **76**, 5920.

dependent on both the temperature and the composition of the mixture. Several investigators have studied dinitrogen trioxide, although the range of stability of the pure compound is not known. Lipscomb and Reed's [3] *X*-ray analyses did not yield a satisfactory structure.

Abel and Proisl,[4] using Bodenstein's values [5] for the dinitrogen tetroxide–nitrogen dioxide equilibrium, evaluated the equilibrium constant for the reaction (1) over a wide

$$N_2O_3 \rightleftharpoons NO + NO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

concentration range at several different temperatures. Extrapolation to zero pressure gave the values at 8·13° and 34·8° as 0·539 and 2·39 atm. respectively. The results yield a value for the heat of reaction of 9600 cal. mole^{-1} (a fuller account which was to have been given. in *Z. phys. Chem.* did not appear). Insufficient data are given [4] to plot the results in the manner now to be described. Verhoek and Daniels [6] studied the equilibrium (1), but the equilibrium constants they obtained (2·105 at 25°, 3·673 at 35°, and 6·880 atm. at 45°; $\Delta H°$ 10,300 cal. mole^{-1}) differed considerably from those of Abel and Proisl.

In view of the considerable discrepancies between the two sets of observations, and since the equilibrium in the gas phase is of considerable analytical importance, it was decided to reinvestigate it.

EXPERIMENTAL

All work was carried out in a vacuum system.

Nitric Oxide.—This was prepared as described by Johnston and Giauque,[7] except that the theoretical quantities of potassium nitrite and potassium iodide were used. The first and the last portion of each distillate from the original material were rejected. Johnston and Giauque reported that they obtained a blue liquid, while Nightingale *et al.*[8] have recently stated that the colour of their product was pale straw-green. We obtained apparently colourless nitric oxide.

Nitrogen Dioxide.—" AnalaR " lead nitrate which had been dried for several days at 200—250° was heated at this temperature *in vacuo*. On raising the temperature to approximately 340° gases were collected in a trap cooled in solid carbon dioxide after passage through a phosphoric oxide column. The product was distilled in an atmosphere of oxygen. After removal of the oxygen the mixture was again distilled, the first and the last fraction being rejected.

An accurately weighed ampoule was partially filled by distillation, sealed, and separated at a previously made constriction. After rigorous cleaning the ampoule was reweighed. This technique was checked several times by using no nitrogen dioxide. The results indicated a high order of reproducibility for the weighings if a standard method of treatment was followed exactly. All joints were carefully greased with I.C.I. " Florube " W grease, so that a minimum quantity came into contact with the nitrogen dioxide.

Apparatus and Technique.—An all-glass apparatus was used as we found that all possible greases either reacted with or absorbed oxides of nitrogen during the experiment. Fluorinated greases appear to be unreactive, but extensive physical sorption occurs. The reaction vessel, *A*, and pressure measuring system are shown in Fig. 1. An ampoule containing nitrogen dioxide was introduced into the internally calibrated tube *B*, together with a steel-in-glass breaker. Tube *B* was subsequently joined to the vacuum line *via* a constriction *C*. The apparatus was continuously pumped for at least 2 days, since it was impracticable to flame out the glassware. By surrounding the projection *D* with liquid air a quantity of nitric oxide could be distilled into the reaction system. The constriction at *C* was sealed after pumping on the nitric oxide for a short while. The nitric oxide was allowed to attain a steady temperature, the pressure was noted, and the nitrogen dioxide ampoule broken. Complete mixing of the gases was ensured by successively freezing them out in *D*, followed by leaving the mixture

[3] Lipscomb and Reed, *Acta Cryst.*, 1953, **6**, 781.
[4] Abel and Proisl, *Z. Elektrochem.*, 1929, **35**, 712.
[5] Bodenstein, *Z. phys. Chem.*, 1922, **100**, 68.
[6] Verhoek and Daniels, *J. Amer. Chem. Soc.*, 1931, **53**, 1250.
[7] Johnston and Giauque, *J. Amer. Chem. Soc.*, 1929, **51**, 3194.
[8] Nightingale, Downie, Rotenberg, Crawford, and Ogg, *J. Phys. Chem.*, 1954, **58**, 1047.

for at least two days to come to equilibrium. Pressures were then measured at temperatures near 5°, 15°, 25°, 35°, and 45°. At the end of the experiment the tube B was cut squarely in the undistorted portion just below C, the distance from a reference point to the cut being noted. The volume of the removed cup, the ampoule, and the magnetic breaker was measured. The internal volume of the main apparatus (at least 1 l.) was eventually found up to the same reference point in B.

Pressures were measured by using a sensitive spiral gauge with a 3-metre optical beam as a null instrument. The double-tube mercury manometer, having a common reservoir, was constructed of Chance's " Veridea " tubing (1·6 cm. internal diam.). The pressure on the spiral gauge was varied by the introduction of dry air, fine adjustment being possible by means of tap G. Pressure readings are expressed in international atmospheres and are accurate to ± 5 × 10⁻⁵ international atmospheres. All weighings were carried out with calibrated weights, and the thermometers were standardised against a previously calibrated ten-junction copper–constantan thermocouple.
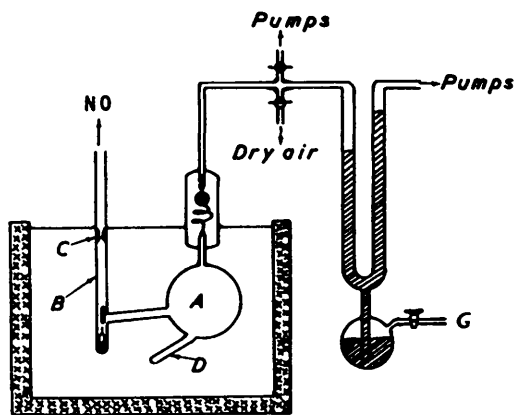

FIG. 1.

DISCUSSION

In a mixture containing only nitrogen dioxide, dinitrogen tetroxide, nitric oxide, and dinitrogen trioxide, equations (2—5) are valid for ideal gases, where p (with symbol in parentheses) is the partial pressure at equilibrium, p^0 is the initial partial pressure $[p^0(N_2O_4)$, no dissociation being assumed], and P = the total pressure at equilibrium.

$$K_1 = p^2(NO_2)/p(N_2O_4) \qquad \cdots \cdots \qquad (2)$$

$$p^0(NO) = p(NO) + p(N_2O_3) \qquad \cdots \cdots \qquad (3)$$

$$2p^0(N_2O_4) = 2p(N_2O_4) + p(NO_2) + p(N_2O_3) \qquad \cdots \cdots \qquad (4)$$

$$P = p(N_2O_4) + p(NO_2) + p(NO) + p(N_2O_3) \qquad \cdots \cdots \qquad (5)$$

From eqns. (5) and (4), $\quad 2p(NO) = 2P - 2p^0(N_2O_4) - p(NO_2) - p(N_2O_3)$

which with eqn. (3) yields $p(NO) = 2P - 2p^0(N_2O_4) - p(NO_2) - p^0(NO)$ (6) (cf. ref. 6)

From eqns. (5), (3), and (2), $p^2(NO_2) + K_1 p(NO_2) + K_1[p^0(NO) - P] = 0 \qquad \cdots \qquad (7)$

Whence for real roots $p(NO_2) = \frac{1}{2}(-K_1 + \sqrt{\{K_1{}^2 + 4K_1[P - p^0(NO)]\}})$

Clearly from (3), (6), and (7) it is possible to evaluate K_2 where

$$K_2 = p(NO) \cdot p(NO_2)/p(N_2O_3)$$

A reaction involving dinitrogen tetroxide would yield an equilibrium constant $K_3 = K_2{}^2/K_1$ and K_3 and K_2 would presumably each have a different dependence on concentration, as pointed out by Verhoek and Daniels. With the two equilibria involved this does not appear to be relevant to the problem.

It is extremely unlikely that any molecular species other than NO, NO_2, N_2O_3, and N_2O_4 is present at equilibrium. This does not exclude the possibility of the presence of structural isomers for N_2O_3 and N_2O_4, although these would not markedly affect the pressure dependence of the results.

The experimental results are given in Table 1 [data for the nitrogen dioxide–dinitrogen

tetroxide equilibrium were calculated from the material and by the method recommended by Giauque and Kemp [9]. It is evident that quite wide variations occur in K_2. These deviations may be due to non-ideality of the gases, sorption, or variations in K_1 with pressure. Although the amount of gas sorbed on the walls of the vessel necessary to form a monolayer would cause errors in the pressure readings only within the experimental

TABLE 1. *Experimental observations on the dinitrogen trioxide equilibrium and calculated equilibrium constants.*

Temp.	A * (atm.)	Vol. (ml.) †	P (atm.)	K_2 (atm.)	Temp.	A * (atm.)	Vol. (ml.) †	P (atm.)	K_2 (atm.)
4.96°	1.48728	1265.5	0.58548	0.374	5.00°	0.50110	1269.1	0.44680	0.478
15.00		(1268.3)	0.63033	0.752	15.01		(1271.9)	0.47492	0.909
25.04	(0.30129)		0.68017	1.34	25.12	(0.36709)		0.50559	1.66
35.08			0.73626	2.29	35.02			0.53658	2.71
45.12			0.79774	3.83	45.10			0.56892	4.48
4.96	1.21744	1263.8	0.56971	0.409					
15.00		(1266.9)	0.61060	0.776	15.00	2.10492	1272.1	0.60501	0.606
25.04	(0.34391)		0.65754	1.43	24.97	(0.12580)	(1274.5)	0.65907	1.12
35.08			0.70769	2.30	35.01			0.72206	1.95
45.12			0.76315	3.76	45.01			0.79228	3.23
4.96	0.84238	1264.5	0.24187	0.435	4.95	1.34501	1273.1	0.34848	0.353
15.00		(1267.6)	0.26480	0.759	14.92		(1275.5)	0.37960	0.692
25.04	(0.05488)		0.29187	1.52	24.96	(0.05856)		0.41736	1.29
					35.12			0.46101	2.26
4.96	0.47498	1271.5	0.67870	0.457	45.12			0.50843	3.79
15.00		(1274.5)	0.71589	0.869					
25.04	(0.63231)		0.75555	1.59	4.95	1.33390	1270.7	0.72332	0.417
35.08			0.79579	2.65	14.97		(1273.1)	0.77215	0.799
45.12			0.83678	4.60	25.04	(0.49548)		0.82707	1.46
5.03	0.53386	1269.2	0.63475	0.476	34.99			0.88559	2.41
15.08		(1272.4)	0.67120	0.911	45.04			0.94984	3.94
25.07	(0.56959)		0.70951	1.61					
35.11			0.74995	2.77	15.00	2.10885	1271.6	0.83070	0.655
45.19			0.79087	4.52	25.01	(0.38256)	(1274.2)	0.89544	1.19
5.05	0.45360	1268.4	0.71440	0.463	35.07			0.96888	2.06
15.03		(1271.4)	0.75387	0.952					
25.07	(0.67577)		0.79364	1.68	14.95	2.22996	1270.9	0.85894	0.670
35.04			0.83449	2.77	25.04	(0.38471)	(1273.3)	0.92652	1.24
45.21			0.87689	4.62	35.05			1.00249	2.16
5.01	0.87667	1268.0	0.79707	0.427					
15.01		(1271.0)	0.84459	0.819	4.99	0.52400	1268.1	0.43329	0.471
25.07	(0.67986)		0.89641	1.49	15.00		(1270.4)	0.46101	0.883
35.08			0.45055	2.49	25.04	(0.34674)		0.49133	1.59
45.08			1.00728	4.04	35.16			0.52313	2.65
					45.05			0.55526	4.49
4.86	0.08535	1268.6	0.26347	0.590	4.86	0.97346	1268.3	0.63796	0.427
15.01		(1270.1)	0.27587	0.921	14.95		(1270.7)	0.68003	0.815
25.04	(0.26059)		0.28880	1.83	25.04	(0.47831)		0.72638	1.48
35.08			0.30098	3.03	35.02			0.77586	2.46
45.12			0.31274	5.12	45.21			0.82918	4.03

* *A*, Mass of N_2O_4 (g.) with the measured pressure of NO at the temperature nearest 25° in parentheses.

† Vol. of cell containing NO, with vol. of cell containing the equilibrium mixture in parentheses.

error, it is possible that the sorbed gases, by affecting the surface of the glass in the spiral, could cause errors in the zero readings of the gauge. The deviations mentioned would be removed on extrapolation to zero pressure. The sorption of the polar molecule NO_2 is likely to be higher than that of any other species present. The results were therefore plotted for K_2 as a function of the partial pressure of nitrogen dioxide, and are shown in Fig. 2. The

⁹ Giauque and Kemp., *J. Chem. Phys.*, 1938, **6**, 40.

FIG. 2. *Equilibrium constant for the dissociation of dinitrogen trioxide as a function of the partial pressure of the nitrogen dioxide.*

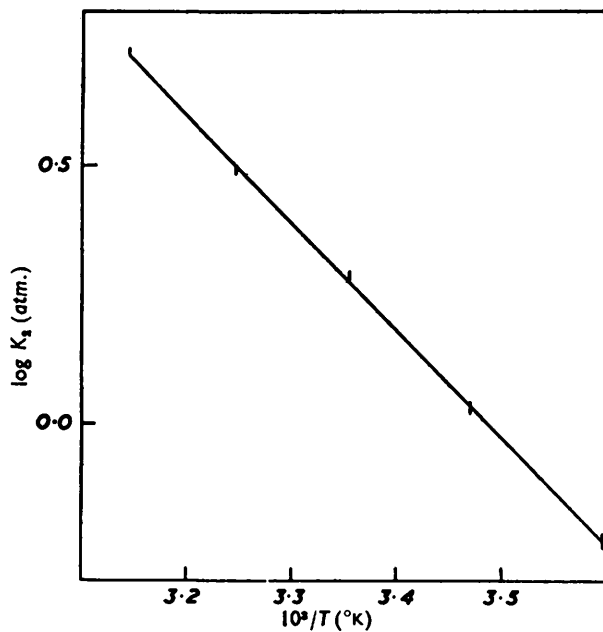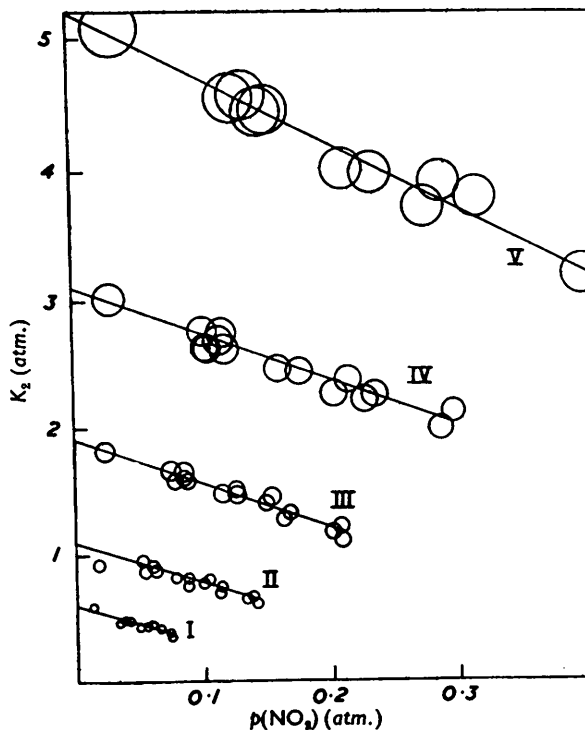I, 5°; II, 15°; III, 25°; IV, 35°; V, 45°

FIG. 3. *The relation between the logarithm of the extrapolated equilibrium constant for the dissociation of dinitrogen trioxide and the reciprocal of the absolute temperature.*

circles represent errors of $\pm 4\%$ from the centre. It is probable that there is a linear relation, all except four of the circles being on the lines which have been drawn (2 of these exceptional points are at extremely low pressures).

Table 2 gives the extrapolated values of K_2 at various temperatures (obtained by the method of least squares) together with the standard deviation σ. These results are plotted in Fig. 3, giving the expected linear relationship between log K_2 and the reciprocal of the absolute temperature. Again, the application of the least-squares method yielded a value of 9527 ± 96 cal. mole^{-1} for the heat of reaction. The corresponding entropy change for the reaction was $33 \cdot 25 \pm 0 \cdot 35$ cal. mole^{-1} deg.$^{-1}$.

TABLE 2. *Extrapolated values of K_2 at various temperatures.*

Temp.	$45 \cdot 00°$	$35 \cdot 00°$	$25 \cdot 00°$	$15 \cdot 00°$	$5 \cdot 00°$
$K_2°$ (atm.)	$5 \cdot 193$	$3 \cdot 097$	$1 \cdot 916$	$1 \cdot 082$	$0 \cdot 595$
σ (atm.)	$\pm 0 \cdot 059$	$\pm 0 \cdot 041$	$\pm 0 \cdot 027$	$\pm 0 \cdot 025$	$\pm 0 \cdot 018$

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