206. *The Formation and Thermodynamic Properties of Nitrous Acid Vapour.*

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The gas-phase equilibrium between nitric oxide, nitrogen dioxide, water, and nitrous acid has been studied at 20°, 40°, 60°, and 80° c. Values of ΔS°_{298} and ΔH°_{298} for the reaction $NO_2 + NO + H_2O \longrightarrow 2HNO_2$ have been calculated from the measured equilibrium constants, and used to evaluate the standard heat of formation and standard entropy of nitrous acid vapour.

When nitric oxide, nitrogen dioxide, and water vapour are mixed in the gas phase, nitrous and nitric acid vapours are formed. As dinitrogen tetroxide and dinitrogen trioxide are also present, the system can be represented by the following equilibria:

$$2NO_2 \underset{-1}{\overset{1}{\rightleftharpoons}} N_2O_4 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$NO + NO_2 \underset{-2}{\overset{2}{\rightleftharpoons}} N_2O_3 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$NO + NO_2 + H_2O \underset{-3}{\overset{3}{\rightleftharpoons}} 2HNO_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$3NO_2 + H_2O \underset{-4}{\overset{4}{\rightleftharpoons}} 2HNO_3 + NO \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

The equilibria (1), (2), and (4) have been extensively studied, and the equilibrium constants have been measured [1,2] or calculated [3] at various temperatures. The changes of the heat content, the free energy, and the entropy are known for each of the six reactions involved. In contrast, little is known about equilibrium (3) and about the thermodynamic properties of nitrous acid vapour, although the reactions (3), (-3) have been used to prepare nitrous acid vapour for spectroscopic studies [4-6] of the molecule. A value for K_3 at 25° was determined experimentally by Wayne and Yost,[7] and was shown by them to be in fair agreement with thermodynamic data on the free energy of formation of nitrous acid in solution. They also showed that the equilibrium is established rapidly at that temperature. The entropy of HNO_2 vapour at 25° was calculated by Jones, Badger, and Moore,[6] the appropriate partition functions being calculated from the molecular constants derived from their infrared spectroscopic studies; their value was later revised.[8] The heat and the free energy of formation of HNO_2 vapour have not previously been measured.

It appeared from Wayne and Yost's data that the equilibrium constant K_3 could be determined accurately at various temperatures about 20° by combining pressure measurements with photometric measurements of the amount of nitrogen dioxide present in suitable mixtures of nitric oxide, nitrogen dioxide, and water vapour. From these values of K_3 the change of heat content and free energy of reaction (3) could be determined, and hence the thermodyanamic properties of nitrous acid vapour evaluated. It was generally possible to choose temperatures and mixture proportions with excess of nitric oxide such that the equilibria (1), (2), and (4) lay well to the left, thus keeping small the corrections for the amounts of dinitrogen trioxide and tetroxide and nitric acid present, with reasonable yields of nitrous acid.

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[1] Verhoek and Daniels, *J. Amer. Chem. Soc.*, 1931, **53**, 1250; Giauque and Kemp, *J. Chem. Phys.*, 1938, **6**, 40.

[2] Beattie and Bell, *J.*, 1957, 1681.

[3] Forsythe and Giauque, *J. Amer. Chem. Soc.*, 1942, **64**, 48.

[4] Porter, *J. Chem. Phys.*, 1951, **19**, 1278.

[5] D'Or and Tarte, *Bull. Soc. roy. Sci. Liége*, 1951, 478.

[6] Jones, Badger, and Moore, *J. Chem. Phys.*, 1951, **19**, 1599.

[7] Wayne and Yost, *J. Chem. Phys.*, 1951, **19**, 41.

[8] Altshuller, *J. Phys. Chem.*, 1957, **61**, 251.

EXPERIMENTAL

Apparatus.—A conventional vacuum-apparatus was used for preparing, storing, and mixing the reactants. The reaction vessel was cylindrical, 20 cm. long and of 3·4 cm. internal diameter, with plane end-windows and a capillary entry tube which entered radially, opposite the mid-point of the axis. The vessel was kept in a water thermostat, and the temperature was controlled to ±0·05° by a Techne Tempunit and read from a calibrated mercury thermometer. Tightly fitting lengths of pressure tubing were placed between the end-windows of the reaction vessel and the windows of the thermostat to prevent the circulating water from disturbing the light used for photometry. The mixing vessel was kept in a thermostat at 73°, and the intermediate connecting tubing was heated electrically to about 80°.

Pressures were measured with a Bourdon gauge to 50 mm. Hg and on a mercury manometer above this pressure. The manometer was previously filled with nitric oxide to near the correct pressure if the mixture involved a corrosive gas. The double-beam photometric system used to measure the concentration of nitrogen dioxide was similar to that developed by Ashmore *et al.*[9] An Ilford 602 filter was used, passing wavelengths between 4500 and 5000 Å.

Nitric oxide was prepared from sodium nitrite solution and dilute sulphuric acid. The initial sample was fractionated, and the product distilled several times through a trap at −119°, and over phosphoric oxide. Nitrogen dioxide was prepared from nitric oxide and oxygen. De-aerated, distilled water was used.

Procedure.—The mixtures were prepared by two different procedures. In the first, nitrogen dioxide was measured into the reaction vessel, and a mixture of chosen pressures of nitric oxide and water vapour was prepared in the mixing vessel. This mixture was left for 20 min. to attain a uniform composition, and then admitted to the reaction vessel. The total pressure in the reaction vessel was measured when no further change occurred in the photometer reading. After 10—30 min., the reaction vessel was evacuated. Nitrogen dioxide was then admitted until the photometer signal equalled that before evacuation, and its pressure was measured. This method of determining the amount of nitrogen dioxide in the equilibrium mixture eliminated any error due to drift of the photometer over the period of mixing. It assumes that absorption of light by any other species can be neglected; this point is discussed later.

In the second method, water vapour was measured into the reaction vessel, and a mixture of nitric oxide and nitrogen dioxide was run in from the mixing vessel. The measurements were made in the same way as in the first method.

A check was made upon the time required for the mixtures to become homogeneous by diffusion by adding a large pressure of oxygen to nitrogen dioxide in the reaction vessel. The concentration of nitrogen dioxide in the end section of the vessel was followed photometrically, with the light beam directed along a diameter of the vessel. It was found that the concentration of nitrogen dioxide could rise to over three times its initial value as the oxygen was admitted, and then fell slowly until after 5 min. the increase in concentration over the initial value was less than 2%. On this basis, a minimum time of 10 min. was allowed for mixing.

DISCUSSION

When the nitric oxide plus water mixtures, containing a mole fraction x of water, were added to nitrogen dioxide in the reaction vessel, the measured quantities were the initial and final pressures $P'_{\mathrm{NO_2}}$ and $P_{\mathrm{NO_2}}$ of nitrogen dioxide, and the total pressure at equilibrium, P_{T}. Then, considering the pressures, and the molar balance of NO, NO_2, and H_2O and the equilibria (1) and (2), we have

$$P_{\mathrm{T}} = P_{\mathrm{NO}} + P_{\mathrm{NO_2}} + P_{\mathrm{N_2O_3}} + P_{\mathrm{N_2O_4}} + P_{\mathrm{HNO_2}} + P_{\mathrm{HNO_3}} + P_{\mathrm{H_2O}}$$

$$P'_{\mathrm{NO_2}} + 2P'_{\mathrm{N_2O_4}} = P_{\mathrm{NO_2}} + 2P_{\mathrm{N_2O_4}} + \tfrac{1}{2}P_{\mathrm{HNO_2}} + \tfrac{3}{2}P_{\mathrm{HNO_3}} + P_{\mathrm{N_2O_3}}$$

$$(1 - x)[P_{\mathrm{H_2O}} + \tfrac{1}{2}P_{\mathrm{HNO_2}} + \tfrac{1}{2}P_{\mathrm{HNO_3}}] = x[P_{\mathrm{NO}} + P_{\mathrm{N_2O_3}} + \tfrac{1}{2}P_{\mathrm{HNO_2}} - \tfrac{1}{2}P_{\mathrm{HNO_3}}]$$

$$P'_{\mathrm{N_2O_4}} = K_1(P'_{\mathrm{NO_2}})^2 \qquad P_{\mathrm{N_2O_4}} = K_1(P_{\mathrm{NO_2}})^2 \qquad P_{\mathrm{N_2O_3}} = K_2P_{\mathrm{NO}}P_{\mathrm{NO_2}}$$

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[9] Ashmore, Levitt, and Thrush, *Trans. Faraday Soc.*, 1956, **52**, 830; Ashmore and Levitt, Seventh Symposium on Combustion, 1959, Butterworths, London, p. 45.

Except where previously defined, the symbol P refers to the partial pressure in the equilibrium mixture. In evaluating P_{NO}, P_{H_2O}, and P_{HNO_3} from these equations, it is convenient first to evaluate approximate values by neglecting the small quantity, P_{HNO_3}, and then to calculate P_{HNO_3} from these approximate values and the equilibrium constant, K_4. The value of P_{HNO_3} can be used to obtain better values for the quantities required, and so on. Experiments at 40° and 80° with water and nitrogen dioxide only had shown that the nitric acid estimated to be formed from a nitrogen balance corresponded closely to that expected if the equilibrium (4) were attained, the equilibrium constant being based on the data of Forsythe and Giauque.[3]

With the second method of preparing the mixtures, a similar set of equations were developed. In solving these, an estimated value of P_{HNO_2} was substituted, giving pressures of the remaining components, which in turn permitted the calculation of a more accurate value of P_{HNO_2}. The values obtained by repetition of this process rapidly converged. To obtain the correct value for the mole fraction x' of nitrogen dioxide in the mixing vessel, it was necessary to allow for the small amounts of N_2O_3 and N_2O_4 also present in the mixture.

In all experiments, the addition of the mixture from the mixing vessel swept into the reaction vessel that portion of the component measured into the reaction vessel which lay in the dead space (about 1% of the total). It was shown that very little of this material diffused back into the dead space, and it was counted as part of the reaction vessel gases.

Examples of composition of equilibrium mixtures.

Expt.	Temp.	P_{NO_2} (mm.)	$P_{N_2O_4}$ (mm.)	$P_{N_2O_3}$ (mm.)	P_{NO} (mm.)	P_{H_2O} (mm.)	P_{HNO_2} (mm.)	P_{HNO_3} (mm.)	K_3 (atm.$^{-1}$)
B7	19·95°	15·50	3·40	8·00	510·5	12·90	13·70	0·041	1·40
D13 ...	80·7	17·70	0·05	0·44	440·8	98·9	10·65	0·039	0·112

There are several other possible sources of error for which it is not possible to make any satisfactory correction.

(*a*) It has been assumed that no species other than NO_2 absorbs light in the wave band used in the photometer. The spectra of gaseous NO, N_2O_4, and HNO_3 are sufficiently well known to reject them as possible absorbers, but there are no data for N_2O_3 in the gas phase. Recent work[10] with solutions of N_2O_3 showed a strong absorption in the ultraviolet region, with a weaker band ($\varepsilon \approx 20$) in the red region. At 4700 Å there is an absorption minimum, with $\varepsilon = 1$. By comparing the absorption spectra of NO_2–N_2O_4 with that of a mixture of NO, NO_2, N_2O_3, and N_2O_4, it was shown that the same general features appear in the gas phase. There is a weak absorption ($\varepsilon \approx 5$) at 7500—8000 Å, and a strong ultraviolet absorption ($\varepsilon > 170$ at 3000 Å) attributed to N_2O_3. However, at 4500—5000 Å, the difference in optical density between the mixtures was less than the possible difference due to errors in measuring the NO_2 pressure. Comparison of the absorption by N_2O_3 in solution and in the gas phase suggests that it is unlikely that $\varepsilon > 1$ for gaseous N_2O_3 at 4700 Å. If ε is taken as 1, then at 20° the value of P_{NO_2} taken for the equilibrium mixture would exceed the correct value by 0·5%, which would result in the reported value of K_3 being about 5% too low. At 40°, the error in K_3 would be 1·4%, falling further at higher temperatures. Owing to the uncertainty of the value of the extinction coefficient, however, no correction was applied.

The absorption of nitrous acid vapour has been observed[4] between 3100 and 3900 Å, and it would not be expected that the system observed could extend to 4700 Å. If nitrous acid absorbed in the photometer region, the quoted results for K_3 would be lower than the true value. The effect would be of a similar magnitude at all temperatures, as the ranges of P_{NO_2} and P_{HNO_2} used did not vary greatly with temperature.

(*b*) The pressure of water vapour used was sometimes close to the saturation value,

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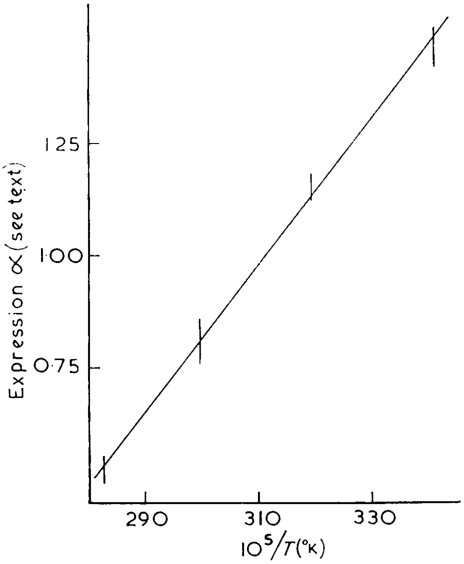
[10] Mason, *J.*, 1959, 1288.

especially at 20°. It is possible that multilayer adsorption of water on the walls can remove a substantial amount from the gas phase, and act as a further source of water when some reacts to give the acids. The result of adsorption would be to make the values of K_3 too high when water was placed in the reaction vessel, and too low when it was in the mixing vessel. No correction can be applied, but the errors are reduced by taking the mean of values obtained by the two methods.

(*c*) There is some uncertainty in the correct value to take for K_2. Beattie and Bell[2] showed that the values change systematically with the pressure of NO_2 present, increasing as the pressure rises. It is not certain whether the values also change with the pressure of NO, other things being equal. The value of K_2 used at 20°, the result of a direct determination in the apparatus used here, was about 6% higher than the value determined by Beattie and Bell for corresponding pressures. The error would not be important at the temperatures higher than 20°.



The relation between α (see text) and the reciprocal of the absolute temperature.

It is clear that these uncertain errors are only likely to affect the value of K_3 at the lower temperatures. Accordingly, the mean value of K_3 at 20° was given a weight of one-half, compared with the mean values at the higher temperatures, in determining the heat of the reaction.

Results.—The mean values of the equilibrium constant K_3 obtained by each method at the various temperatures, together with the standard deviation of the mean, σ, and the number of experiments on which the results are based are given in the following Table.

	NO and NO_2 pre-mixed			NO and H_2O pre-mixed			All expts.	
Temp.	K_3 (atm.$^{-1}$)	σ (atm.$^{-1}$)	No. of expts.	K_3 (atm.$^{-1}$)	σ (atm.$^{-1}$)	No. of expts.	K_3 (atm.$^{-1}$)	σ (atm.$^{-1}$)
19·95°	1·60	0·12	8	1·51	0·19	9	1·56	0·16
39·90	0·613	0·032	6	0·659	0·045	9	0·641	0·046
60·50	0·258	0·028	11	0·233	0·028	5	0·250	0·030
80·65	0·110	0·010	5	0·114	0·005	5	0·112	0·008

In determining the heat of reaction, allowance was made for the variation of ΔH with temperature due to the different, and varying, specific heats of reactants and products.[8,11,12] If the difference in specific heats, ΔC_p°, over the temperature range 20—80° is put in the approximate form $\Delta C_p^\circ = a + bT$, the slope of a plot of

$$\left\{\log K_3 - \frac{a}{\boldsymbol{R}} \log \frac{T}{100} - \frac{bT}{2 \times 2{\cdot}303 \times \boldsymbol{R}}\right\} \equiv \{\alpha\}$$

against $1/T$ is

$$-\left\{\frac{\Delta H^\circ_{298\cdot2} - 298{\cdot}2a - \tfrac{1}{2}b \times 298{\cdot}2^2}{2{\cdot}303\,\boldsymbol{R}}\right\}$$

The results are shown plotted in this manner in the diagram. The straight line fitted by the least-mean-squares method corresponded to a heat of reaction $\Delta H^\circ_{298\cdot2}$ of -9057 ± 320 cal. mole^{-1}, and an entropy change for the reaction $\Delta S^\circ_{298\cdot2}$ of $-29{\cdot}89 \pm 1{\cdot}30$ e.u.

Combining these values with the heats of formation and the standard entropies [8,11] for NO, NO_2, and H_2O, we obtain the following values for nitrous acid vapour:

Standard entropy, $S^\circ_{298\cdot2} = 61{\cdot}46 \pm 0{\cdot}65$ cal. mole^{-1} deg.$^{-1}$;
Standard heat of formation, $\Delta H^\circ_{298\cdot2} = -18{\cdot}58 \pm 0{\cdot}20$ kcal. mole^{-1};
Standard free energy of formation, $\Delta G^\circ_{298\cdot2} = -10{\cdot}81 \pm 0{\cdot}04$ kcal. mole^{-1}.

The errors quoted refer to those originating from this work only.

Both the *cis*- and the *trans*-form of nitrous acid exist in the gas phase, with an energy difference of about 500 cal., and an energy barrier of interconversion estimated [6] at 12 kcal. The entropies of each form have been calculated [8] from spectroscopic data. The entropy of mixing appropriate to the relative amounts of *cis*- and *trans*-forms at 25° being used, the spectroscopic value of the entropy of the equilibrium mixture is 60·77 e.u. The second-law value determined above is in reasonable agreement with this third-law value.

We thank Drs. J. N. Agar and B. A. Thrush for helpful discussions, and the Department of Scientific and Industrial Research for a Research Studentship (to B. J. T.).

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[*Received, September* 21*st*, 1960.]

[11] " Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Stand., Washington, Circular No. 500, 1952.

[12] Johnston and Chapman, *J. Amer. Chem. Soc.*, 1933, **55**, 153; Gordon, *J. Chem. Phys.*, 1934, **2**, 65.