

## The Free Energy and Entropy of Nitrosyl Chloride

Francis P. Jahn

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## The Free Energy and Entropy of Nitrosyl Chloride

FRANCIS P. JAHN

Department of Chemistry, New York University, University Heights, New York, N. Y.

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Using the harmonic oscillator rigid rotator approximation to the partition function of nitrosyl chloride, the values of the free energy function,  $(F^0 - E_0^0)/T$ , and the entropy,  $S^0$ , have been calculated for the ideal gas from 298.1°K to 1000°K at fifty degree intervals. By comparison with the equilibrium data for the dissociation of nitrosyl chloride,  $\Delta E_0^0$  is found to be  $15,510 \pm 53$  cal. It is found necessary to assume an electronic weight of four for the ground state. Although the calculated equilibrium constants agree fairly well with experiment, a definite trend in the deviations cannot be satisfactorily explained.

IN the course of the determination of the entropy of  $N_2O_4$  from the third law value of the entropy of the  $NO_2 - N_2O_4$  equilibrium mixture, Giauque and Kemp<sup>1</sup> found it necessary to calculate the product of the moments of inertia of the  $NO_2$  molecule in an indirect manner. Using the approximate moments of inertia obtained from electron diffraction measurements, they calculated statistically the free energy of  $NO_2$  referred to the lowest vibrational level at 0°K. By combination of this result with the similar quantities for nitric oxide of Johnston and Chapman and those for oxygen of Johnston and Walker, and the equilibrium data of Bodenstein and co-workers for the dissociation of nitrogen dioxide into nitric oxide and oxygen, Giauque and Kemp were able to verify quite definitely a previously assigned *a priori* weight of two for the ground state of the nitrogen dioxide molecule. They were then able to calculate accurately a value of the product of the moments of inertia which gave a constant  $\Delta E_0^0$  over a wide temperature range. Since the resulting product of the moments of inertia is close to the approximate value obtained from electron diffraction measurement, this work constitutes a check on the accuracy of the equilibrium data of Bodenstein and co-workers.

In the case of nitrosyl chloride the results of electron diffraction measurements are more readily capable of interpretation than those for nitrogen dioxide.<sup>2</sup> It appeared to the writer, therefore, that with the accurate knowledge of the dimensions of nitrosyl chloride and the

assignment of the fundamental vibration frequencies of Bailey and Cassie,<sup>3</sup> it should be possible to check directly the experimental measurements<sup>4, 5</sup> of the nitrosyl chloride dissociation equilibrium. The free energy of an asymmetrical top molecule referred to the lowest vibrational level at 0°K, with the ideal gas at a pressure of one atmosphere as the standard state is:<sup>1</sup>

$$\begin{aligned} (F^0 - E_0^0)/T = & -3/2R \ln M - 4R \ln T \\ & - R/2 \ln I_1 I_2 I_3 - R \ln p_e + R \ln \sigma \\ & - 257.401 + R \sum_{i=1}^{i=3} \ln [1 - \exp(-h\nu_i/kT)], \quad (1) \end{aligned}$$

where  $I_1, I_2, I_3$  are the principal moments of inertia,  $p_e$  is the multiplicity of the ground state, and  $\sigma$  is the symmetry number, which is equal to unity for nitrosyl chloride. Unlike nitrogen dioxide, nitrosyl chloride is not an "odd" molecule; hence in the absence of contradictory evidence  $p_e$  is taken equal to unity.

Ketelaar and Palmer<sup>2</sup> give the following results for the dimensions of nitrosyl chloride:  $Cl-O = 2.65 \pm 0.01$  Å,  $Cl-N = 1.95 \pm 0.01$  Å,  $N-O = 1.14 \pm 0.02$  Å, and the  $O-N-Cl$  angle  $= 116 \pm 2^\circ$ . If one takes the plane of the molecule as the  $x-y$  plane, and the  $x$  axis through the center of gravity parallel to the  $O-Cl$  distance, the resulting moments of inertia are:  $I_x = 1.04 \times 10^{-39}$  g cm<sup>2</sup>,  $I_y = 14.5 \times 10^{-39}$  g cm<sup>2</sup>,  $I_z = 15.5$

<sup>3</sup> Bailey and Cassie, Proc. Roy. Soc. (London), **A145**, 336 (1934).

<sup>4</sup> Trautz and Wachenheim, Zeits. f. anorg. allgem. Chemie **97**, 241 (1916).

<sup>5</sup> Dixon, Zeits. f. physik. Chemie, Bodenstein Festband, 679 (1931).

<sup>1</sup> Giauque and Kemp, J. Chem. Phys. **6**, 40 (1938).

<sup>2</sup> Ketelaar and Palmer, J. Am. Chem. Soc. **59**, 2629 (1937).

TABLE I. Free energy of nitrosyl chloride assuming electronic weight of unity.

$T^{\circ}\text{K}$	$-(F^0 - E_0^0)/T \text{ NOCl}$
450	56.472 cal./mole— $^{\circ}\text{K}$
500	57.422
550	58.298
600	59.113
650	59.876
700	60.594
750	61.260

$\times 10^{-39} \text{ g cm}^2$ ,  $I_x I_y I_z = 2.34 \times 10^{-115} \text{ g}^3 \text{ cm}^6$ . A transformation to principal axes introduces only a small change;  $I_1 I_2 I_3 = 2.06 \times 10^{-115} \text{ g}^3 \text{ cm}^6$ . The frequency assignment of Bailey and Cassie<sup>3</sup> is:  $\nu_1 = 1832 \text{ cm}^{-1}$ ,  $\nu_2 = 633 \text{ cm}^{-1}$ ,  $\nu_3 = 923 \text{ cm}^{-1}$ . The molecular weight is taken as 65.465. The errors to be expected from nonconsideration of the several isotopic species of nitrosyl chloride are negligible.<sup>6</sup> Following general usage, the values of the fundamental constants used are those listed in *International Critical Tables*.

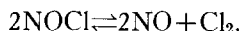
Upon introduction of known quantities Eq. (1) becomes

$$-(F^0 - E_0^0)/T = 4R \ln T - R \sum_{i=1}^{i=3} \ln [1 - \exp(-h\nu_i/kT)] + 7.521. \quad (2)$$

The resulting values for the free energy are listed in Table I.

#### COMPARISON WITH EXPERIMENT

With the aid of the accurate free energy functions for nitric oxide of Johnston and Chapman,<sup>7, 8</sup> and for chlorine of Giauque and Overstreet,<sup>9</sup> and the data of Table I, it is possible to calculate the quantity  $\Delta(F^0 - E_0^0)/T$  for the equilibrium:



Values of this quantity appear in Table II.

<sup>6</sup> Stevenson and Beach, J. Chem. Phys. **6**, 25 (1938).

<sup>7</sup> Johnston and Chapman, J. Am. Chem. Soc. **55**, 153 (1933).

<sup>8</sup> The correction applied by Witmer, J. Am. Chem. Soc. **56**, 2229 (1934) to the nitric oxide free energy function of Johnston and Chapman was not used. Johnston and Chapman used a slightly high value for the nitric oxide doublet separation, but the magnitude of the correction is negligible for the present purpose.

<sup>9</sup> Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).

Then:

$$\Delta E_0^0/T = -R \ln K_p - \Delta(F^0 - E_0^0)/T. \quad (3)$$

The equilibrium has been investigated by Trautz and Wachenheim<sup>4</sup> and more recently by J. K. Dixon.<sup>5</sup> In both cases the measurements of the extent of reaction were based upon pressure changes alone. The two sets of data are in good agreement. Using Dixon's equation,<sup>10</sup> which reproduces his equilibrium constants well over a range of almost three hundred degrees, the writer has calculated  $\Delta F^0/T = -R \ln K_p$  at fifty degree intervals over the range of the experimental measurements. Then  $\Delta E_0^0/T$  was calculated by Eq. (3). The units are cal./ $^{\circ}\text{K}$  or calories as the case may be.

The values of  $\Delta E_0^0$  in column 5 of Table II show a very marked rise with temperature. If a temperature independent quantity  $\delta$  is chosen such that when values of  $\Delta E_0^0/T$  at 450 $^{\circ}\text{K}$  and 750 $^{\circ}\text{K}$  are diminished by  $\delta$  the resulting values for  $\Delta E_0^0$  are equal, then  $\delta$  is found to be 5.673. If each  $\Delta E_0^0/T$  value is decreased by 5.673, the average  $\Delta E_0^0$  resulting is  $15,412 \pm 52$  cal.

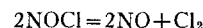
The fact that the quantity 5.673 is independent of temperature leads one to believe that the source of discrepancy is not the equilibrium data. One is therefore led to a consideration of the temperature independent terms of the free energy Eq. (1). The electron diffraction measurements are reliable insofar as the distances are

TABLE II. Calculation of  $\Delta E_0^0$  for reaction  $2\text{NOCl} = 2\text{NO} + \text{Cl}_2$  from data of Dixon.

$T^{\circ}\text{K}$	$\Delta F^0/T = -R \ln K_p$	$-\Delta(F^0 - E_0^0)/T$	$\Delta E_0^0/T$	$\Delta E_0^0$
450	12.023	28.103	40.126	18,050
500	7.959	28.499	36.458	18,230
550	4.677	28.945	33.622	18,500
600	1.985	29.272	31.257	18,750
650	-0.250	29.558	29.308	19,040
700	-2.121	29.799	27.678	19,360
750	-3.700	30.045	26.345	19,750

<sup>10</sup> It might be noted in passing that an error appears on page 686 of the paper by Dixon;  $\Delta F_{298}^0$  should equal 9850 rather than 8600 cal. Then  $\Delta S_{298}^0$  is equal to 29.4 instead of 33.6 cal./degree.

These quantities are for the equilibrium:



treated according to the Lewis and Randall convention. This change will alter some of the calculated results of Leermakers and Ramsperger in their work on the nitrosyl chloride, methyl alcohol, hydrogen chloride, methyl nitrite equilibrium. J. Am. Chem. Soc. **54**, 1837 (1932).

concerned. Ketelaar and Palmer<sup>2</sup> state, however, that because of the very nearly equal scattering powers of the nitrogen and oxygen atoms they were unable to distinguish between the structures N—O—Cl and O—N—Cl, though the latter structure was felt to be in better accord with chemical evidence. Since this question was not definitely settled, the moments of inertia were also calculated for the N—O—Cl structure. It was found, however, that the results did not differ appreciably from those obtained for the O—N—Cl configuration.

The possibility remains that the electronic weight  $p_e$  was incorrectly assumed equal to unity. Actually if a weight of four is assumed, the values of  $\Delta E_0^0/T$  are diminished by the quantity  $2R \ln 4$  or 5.509. This compares favorably with the value 5.673 found empirically. If the values of  $\Delta E_0^0/T$  are recalculated using  $p_e=4$ , the results in Table III are obtained.

The deviations from the average value of  $\Delta E_0^0$  are seen to be systematic. It may be noted that a systematic trend might be expected to result from the neglecting of gas imperfection and the anharmonicity of the oscillations. The frequencies are possibly not quite correct since Bailey and Cassie,<sup>3</sup> using moderate resolving power found it difficult to locate exactly the band heads. Errors of this sort are not expected to be serious since the vibrational contribution to the free energy is quite small. The same is true of vibration-rotation interaction. The multiplicity of the ground level of the nitrosyl chloride seems therefore to be fixed quite definitely as four. It would be valuable if this quantity could be obtained by an independent method, such as for example the measurement of the magnetic susceptibility of the vapor.<sup>1</sup>

Using the average value of  $\Delta E_0^0$  given above,

TABLE III.  $\Delta E_0^0$  for reaction  $2\text{NOCl} = 2\text{NO} + \text{Cl}_2$  assuming  $p_e=4$ .

$T^\circ\text{K}$	$\Delta E_0^0/T$	$\Delta E_0^0$
450	34.617 cal./°K	15,572 cal.
500	30.949	15,475
550	28.113	15,462
600	25.748	15,449
650	23.799	15,469
700	22.169	15,518
750	20.836	15,627
		$(\Delta E_0^0)_{\text{Av}} = 15,510 \pm 53 \text{ cal.}$

TABLE IV. *Equilibrium constants for reaction*  
 $2\text{NOCl} = 2\text{NO} + \text{Cl}_2$ .

$T^\circ\text{K}$	$K(\text{ATMOS.})$	$K(\text{DIXON})(\text{ATMOS.})$
450	$2.540 \times 10^{-3}$	$2.36 \times 10^{-3}$
500	$1.757 \times 10^{-2}$	$1.82 \times 10^{-2}$
550	$9.093 \times 10^{-2}$	$9.5 \times 10^{-2}$
600	$3.506 \times 10^{-1}$	$3.68 \times 10^{-1}$
650	1.099	1.13
700	2.926	2.91
750	6.964	6.44

some equilibrium constants have been calculated. These and the corresponding values from Dixon's equation are given in Table IV. Except for the extreme temperatures the agreement is good. The systematic trend observed earlier in the  $\Delta E_0^0$  values of course occurs here also. Apart from the character of this trend, the deviations are within experimental error<sup>5</sup> ( $\pm 5$  percent) with the exception of the value at 750°K.

#### FREE ENERGY AND ENTROPY

With introduction of  $p_e=4$ , the free energy Eq. (3) becomes

$$-(F^0 - E_0^0)/T = 4R \ln T$$

$$-R \sum_{i=1}^{i=3} \ln [1 - \exp(-h\nu_i/kT)] + 10.275. \quad (4)$$

The entropy expression arising upon differentiating with respect to the temperature is:

$$S^0 = 4R \ln T + R \sum_{i=1}^{i=3} \left( \frac{h\nu_i/kT}{\exp(h\nu_i/kT) - 1} - \ln [1 - \exp(-h\nu_i/kT)] \right) + 10.275 + 4R. \quad (5)$$

In Table V appear values for the free energy and entropy of nitrosyl chloride calculated by means of Eqs. (4) and (5), respectively. One may now calculate the changes in the standard thermodynamic quantities at 298.1°K for the reaction  $2\text{NOCl} = 2\text{NO} + \text{Cl}_2$ .

The value of  $(F^0 - E_0^0)/T$  for nitric oxide at 298.1°K is  $-42.985$ , and that for  $S^0_{298.1}$  is 50.35.<sup>7</sup> Those for chlorine are, respectively,  $-45.951$  and 53.31,<sup>9</sup> the units being cal./mole-°K. Using the value of  $-(F^0 - E_0^0)/T$  from Table V one

finds for the reaction  $2\text{NOCl} = 2\text{NO} + \text{Cl}_2$

$$\Delta(F^0 - E_0^0)/T = -20.569.$$

Since  $\Delta E_0^0 = 15,510 \pm 53$  cal.,

$$\Delta F_{298.1}^0 = (298.1)(-20.569)$$

$$+ 15,510 = 9378 \pm 60 \text{ cal.},$$

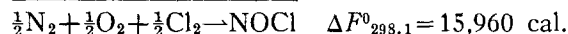
$$\Delta S_{298.1}^0 = 2(50.35) + 53.31$$

$$- 2(64.04) = 25.93 \text{ cal./}^\circ\text{K.},$$

$$\Delta H_{298.1}^0 = 9378 + (298.1)(25.93) = 17,108 \text{ cal.}$$

These and the values derived from Dixon's equation are recorded in Table VI. The use of this equation for calculations at 298.1°K amounts simply to an extrapolation of over a hundred degrees below the lowest experimental temperature; and such discrepancies as are found are to be expected.

Finally the standard free energy, entropy and heat of formation of nitrosyl chloride may be found.



The entropies of  $\text{N}_2^{11}$ ,  $\text{Cl}_2^9$  and  $\text{O}_2^{12}$  at 298.1°K

TABLE V. Free energy and entropy of nitrosyl chloride.

$T^\circ\text{K}$	$-(F^0 - E_0^0)/T \text{ CAL./MOLE } -^\circ\text{K}$	$S^0 \text{ CAL./MOLE } -^\circ\text{K}$
298.1	55.676	64.04
300	55.730	64.10
350	57.033	65.58
400	58.187	66.92
450	59.226	68.15
500	60.176	69.28
550	61.052	70.34
600	61.867	71.32
650	62.630	72.24
700	63.348	73.12
750	64.014	73.93
800	64.671	74.72
850	65.284	75.46
900	65.870	76.17
950	66.430	76.85
1000	66.967	77.50

<sup>11</sup> Giauque and Clayton, J. Am. Chem. Soc. **55**, 487<sup>5</sup> (1933).

<sup>12</sup> Giauque and Johnston, J. Am. Chem. Soc. **51**, 2300 (1929).

TABLE VI. Data for reaction  $2\text{NOCl} = 2\text{NO} + \text{Cl}_2$  and for formation of nitrosyl chloride  $2\text{NOCl} = 2\text{NO} + \text{Cl}_2$ .

	THIS RESEARCH	BY EQUATION OF DIXON
$\Delta F_{298.1}^0$	9378 cal.	9850 cal.
$\Delta S_{298.1}^0$	25.93 cal./deg.	29.4 cal./deg.
$\Delta H_{298.1}^0$	17,108 cal.	18,600 cal.
$\frac{1}{2}\text{N}_2 + \frac{1}{2}\text{O}_2 + \frac{1}{2}\text{Cl}_2 \rightarrow \text{NOCl}$		
$\Delta F_{298.1}^0$	15,960 cal.	
$\Delta S_{298.1}^0$	-10.03 cal./deg.	
$\Delta H_{298.1}^0$	12,970 cal.	

are, respectively: 45.79, 53.31, 49.03 cal./deg. per mole. From Table V  $S_{298.1}^0$  for nitrosyl chloride is 64.04 cal./deg. per mole.

Then

$$\begin{aligned} \Delta S_{298.1}^0 &= 64.04 - \frac{1}{2}(45.79 + 49.03 + 53.31) \\ &= -10.03 \text{ cal./deg.}, \end{aligned}$$

$$\begin{aligned} \Delta H_{298.1}^0 &= \Delta F_{298.1}^0 + (298.1)\Delta S_{298.1}^0 \\ &= 15,960 + (298.1)(-10.03) = 12,990 \text{ cal.} \end{aligned}$$

#### THE ELECTRONIC WEIGHT

If the electron structure of nitrosyl chloride is written down, it is seen that two electron pairs must be shared by the nitrogen and oxygen atoms. This case is analogous to that of the oxygen molecule. Reasoning further by analogy it would seem likely that the ground state of the nitrosyl chloride molecule would be triple, corresponding to parallel orientation of the spins of two electrons, and that there would be a singlet state not far above the ground level. If the energy separation of the states,  $\Delta$ , is small compared to  $kT$ , the electronic partition function becomes effectively equal to four with a small temperature dependence. Thus

$$Z_{\text{elec}} = 3 + \exp(-\Delta/kT) \cong 4 - \Delta/kT + \dots$$

Unfortunately the experimental data are not sufficiently accurate to permit of the determination of this energy separation. It may be said, however, that the data are so much better in accord with a weight of four than with a weight of three that the latter possibility seems definitely excluded.