I.   The Equilibrium Dissociation and Thermodynamic Constants
of Nitrosyl Chloride - Comparison with Spectroscopic Data.

II.   The Diamagnetism of Gaseous Nitrosyl Chloride.

III. The Thermodynamic Constants of Bromine Chloride.
The Equilibrium Reaction between Nitric Oxide, Bromine,
Chlorine, Nitrosyl Bromide and Chloride, and Bromine Chloride.

Thesis by

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Introduction

The compound, bromine chloride, has caused considerable discussion ever since it was first reported by Balard in 1826, and over a century elapsed before Barratt and Stein (1929) showed beyond doubt that the compound actually existed. Immediately, numerous experiments were made in order to determine its dissociation constant at room temperature. Due to difficulties inherent in purely chemical methods of attacking the problem, all of the investigations were limited to light absorption methods. Although most of the results were in fair agreement, the possibility still existed that some unforseen error might be common to all. Just before the present work was undertaken, Jellinek and Schutza (1936) reported a value for the constant at 800° C., obtained through the study of two phase equilibria. Since no results had been obtained between these extremes of temperature, the data did not suffice to evaluate the dissociation constant as function of the temperature.

The chief difficulty in determining the degree of dissociation of bromine chloride lies in the fact that the dissociation is not evidenced by a change in pressure. Professor Yost and co-workers had previously determined that the dissociation of nitrosyl bromide and nitrosyl chloride, acting as auxiliary equilibria, would permit the evaluation of the dissociation constants of bromine chloride throughout a reasonable range of temperature. The auxiliary equilibrium constants were known, but not over the same temperature range. Professor Yost and Blair had determined those for nitrosyl bromide from 25° to 225° C., whereas Dixon had obtained those for nitrosyl chloride from about 200° to 425°. Since a temperature range of from about 100° to 225° was quite suitable, and it was believed not sufficiently accurate to extrapolate Dixon's results, the investigation of the "Thermodynamic Constants of Nitrosyl Chloride" was undertaken.

The results of the equilibrium measurements of nitrosyl chloride afforded considerable interest. The discrepancy between the spectroscopic and experimental entropy changes, as had been disclosed by Jahn, was again observed and a reasonable explanation was found. In order to test the possibility that gaseous nitrosyl chloride exists in a triplet ground state, as suggested by Jahn as a possible explanation of the discrepancy, the magnetic susceptibility of gaseous nitrosyl chloride was measured.

The auxiliary equilibrium constants, combined with measurements of the dissociation of bromine chloride in the presence of nitric oxide, yielded satisfying results concerning the dissociation constants of bromine chloride.

The author feels that the completion of the research has well repaid the effort and wishes to express his appreciation for the excellent supervision and guidance by Professor Don M. Yost.

The Equilibrium Dissociation and Thermodynamic Constants of Nitrosyl Chloride. Comparison with Spectroscopic Data

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Careful measurements of the equilibrium dissociation of nitrosyl chloride into nitric oxide and chlorine have been made in the temperature range 100–220°. Pressure-temperature measurements at 0°–100° on mixtures of nitrosyl chloride and nitric oxide were made and from them the second virial coefficients of nitrosyl chloride gas were calculated. These vary from -389 cm³/mole at 0° to -196 cm³/mole at 100°. The virial coefficients were used to correct the measured equilibrium constants to those for perfect gases. Equations for free energy, entropy and heat content changes accompanying the dissociation were derived as functions of the temperature. The experimentally found entropy changes for the reaction were found to be less than those calculated from spectroscopic data by 3.61 ± 0.3 cal./deg. To attain agreement, the spectroscopic entropy of nitrosyl chloride must be increased by 1.8 cal./deg., and this was attained by assuming that an observed infra-red frequency at 923 cm⁻¹ is a combination, $633 + 290$ cm⁻¹. For the reaction $2NOCl(g) = 2NO(g) + Cl_2(g)$, $\Delta F°_{298} = 9,720 \pm 60$ cal., $\Delta S°_{298} = 28.0 \pm 0.5$ cal./deg. $\Delta H°_{298} = 18,060 \pm 200$ cal. $S°_{298}(NOCl) = 63.0 \pm 0.3$ cal./deg.

INTRODUCTION

THE dissociation of nitrosyl chloride, NOCl, into nitric oxide and chlorine under equilibrium conditions has been studied by several investigators, but only the work of Dixon[1] lays claim to any accuracy. Dixon's results are subject to some uncertainties in the temperature scale

($\pm 2°$), the measurements, and the effect of gas imperfections, so that comparisons with the thermodynamic quantities calculated from molecular and spectroscopic data, while suggestive, are not altogether satisfying. Recently, and after the present investigation was nearly completed, Jahn,[2] employing the electron diffraction results

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[1] Dixon, Zeits. f. physik. Chemie Bodenstein Festband, 679 (1931).

[2] Jahn, J. Chem. Phys. **6**, 335 (1938).

of Ketelaar and Palmer[3] and the infra-red spectrum determined by Bailey and Cassie,[4] showed that between the predictions of theory and Dixon's measurements there is a discrepancy that seems definitely greater than that caused by errors in the measurements. To account for the discrepancy, Jahn suggested that nitrosyl chloride might exist in a triplet normal state and perhaps also a low lying singlet state so that its calculated entropy could be increased by $R \ln 4$. He made the justifiable assumption that the difficulty does not arise from a lack of precise knowledge concerning nitric oxide and chlorine; the spectroscopic and thermal data for nitric oxide have been analyzed carefully by Johnston and Giauque,[5] Johnston and Chapman,[6] and Johnston and Weimer.[7] The assumption of a triplet state requires that the substance be paramagnetic. Although liquid nitrosyl chloride is known to be diamagnetic,[8] Beeson and Coryell[9] made further experiments on the gas and found it to be diamagnetic also. Accordingly no degeneracy of the kind associated with paramagnetism can be invoked in the case of gaseous nitrosyl chloride.

In the present paper are described the results of experiments on the equilibrium reaction

$$2NOCl(g) = 2NO(g) + Cl_2(g) \qquad (1)$$
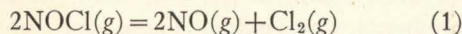
in the temperature range 100°–220°C. In order to make the comparison of the results with theory significant, very pure materials were used and accurate measurements were made. Since the gases are not perfect, additional experiments were made to determine the magnitude of the imperfections. As will be shown below, these accurate measurements are not in accord with the predictions of the theory unless one is justified in giving a different interpretation to the infra-red absorption spectrum than that offered by Bailey and Cassie.

[3] Ketelaar and Palmer, J. Am. Chem. Soc. **59**, 2629 (1937).
[4] Bailey and Cassie, Proc. Roy. Soc. **A145**, 336 (1934).
[5] Johnston and Giauque, J. Am. Chem. Soc. **51**, 3194 (1929).
[6] Johnston and Chapman, J. Am. Chem. Soc. **55**, 153 (1933).
[7] Johnston and Weimer, J. Am. Chem. Soc. **56**, 625 (1934).
[8] Wilson, J. Am. Chem. Soc. **56**, 747 (1934).
[9] Beeson and Coryell, J. Chem. Phys. **6**, 656 (1938).

PREPARATION OF MATERIALS

Chlorine. Tank chlorine was purified as follows. The gas was passed into ice-cold distilled water until most of the latter had been converted into chlorine hydrate, $Cl_2 \cdot 8H_2O$. The temperature was then raised to about 10°, and the chlorine evolved, after passing through reagent grade anhydrous calcium chloride, was condensed into weighed glass capsules. The apparatus used was entirely of glass and the chlorine did not come in
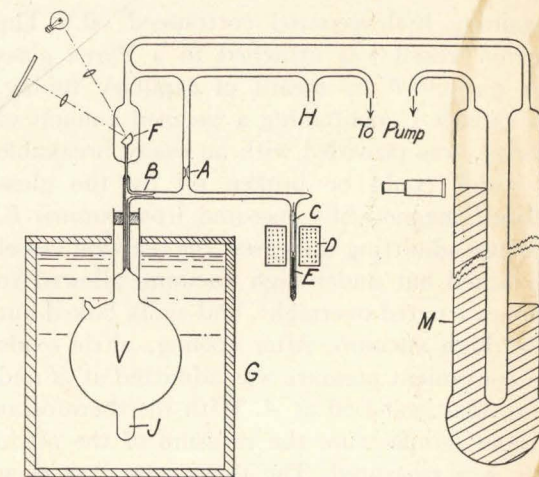

FIG. 1. Reaction vessel and auxiliary apparatus, (not to scale).

contact with rubber or other organic substances. The first portions of chlorine were rejected. Analysis showed that the final product in the sealed glass capsules contained less than 0.1 percent of hydrogen chloride.

Nitric Oxide. The nitric oxide was prepared by a slight modification of the method described by Johnston and Giauque.[5] The gas was stored at about atmospheric pressure in flasks which had been carefully baked out under vacuum for several hours.

EXPERIMENTAL METHODS, PRECISION OF MEASUREMENTS AND CORRECTIONS

Apparatus and procedure

The apparatus[10] is shown diagrammatically in Fig. 1. V is a Pyrex glass reaction vessel of 1049.7 ml capacity at 20°C. G is a thermostat

[10] Blair, Brass and Yost, J. Am. Chem. Soc. **56**, 1916 (1934).

TABLE I. *Initial amounts and pressures of reactants. Volume of the reaction vessel, 1049.7 ml: volume of the dead space, 2.3 ml: volume of the side arm, 23.8 ml.*

| RUN | WT. Cl$_2$ g | NITRIC OXIDE | | | APPROX. MOLE RATIO NO/Cl$_2$ |
		PRESSURE INT. cm Hg AT 0°	TEMP. °C	VOL. ml	
III	0.7397	40.51	19.95	1075.8	2.29
IV	0.8518	30.59	18.88	1075.8	1.50
V	0.7611	37.58	22.00	1075.8	2.04

containing hydrogenated cottonseed oil.[11] The reaction vessel was attached to a Pyrex glass click gauge[12] F by means of capillary tubing. The capsule C, containing a weighed amount of chlorine, was provided with an easily breakable tip which could be broken off by the glass enclosed, magnetically operated, iron hammer E.

Before admitting the gases, the reaction vessel was baked out under high vacuum, allowed to stand evacuated overnight, and again baked out under high vacuum. After cooling, nitric oxide at a convenient pressure was admitted at H and the system sealed off at A. With the thermostat at room temperature the pressure of the nitric oxide was measured. The thermostat was then removed and the nitric oxide condensed by means of liquid air into the tube J. The chlorine C was frozen by means of liquid air and the tip of the capsule broken. On removing the liquid air the chlorine vaporized and condensed in the tube J. Finally the side arm was sealed off at B, and the nitric oxide and chlorine were allowed to vaporize into the reaction vessel.

The volumes of the side arm, 23.8 ml, and the click gauge and capillary tubing, 2.3 ml, were determined at appropriate times and were taken into account in calculating the amount of nitric oxide in the reaction vessel.

The temperature of the thermostat was maintained constant to within ±0.1° by means of a glass-enclosed mercury thermoregulator which contained hydrogen in the space where electrical contact was made or broken. No fouling of the mercury surface occurs in such a regulator if it is carefully freed from oxygen by heating under vacuum before admitting the hydrogen.

Equilibrium pressure measurements were made as follows. Beginning at 100° the temperature of the thermostat was maintained constant for several hours until it was certain that the pressure in the reaction vessel was undergoing no further change. This pressure was then measured. The temperature of the thermostat was raised 10° for one hour, then lowered to the original temperature, and the pressure again measured after it had become constant. This procedure was followed at 10° intervals in proceeding to higher temperatures. In proceeding down the temperature scale, equilibrium was again approached from both the high and low temperature side at each temperature chosen for measurements.

It was found easy to bring the thermostat to any predetermined temperature, and this made it possible, in going down the temperature scale, to carry out measurements at the same temperatures used when going up the scale. Accordingly, for each temperature, four final pressure measurements were made. These did not differ by more than 0.02 cm. The same temperatures were also chosen for the different runs.

Precision of measurements

The thermoregulator maintained the temperature of the thermostat constant to within ±0.1°. Temperatures were measured to ±0.05° with mercury thermometers which were calibrated periodically against thermometers from the National Bureau of Standards.

The mercury manometer used had an inside diameter of 2.15 cm. It was enclosed in a case whose front and sides were, respectively, of plate and window glass. Two thermometers served to determine the temperature of the mercury and of the air in the nonevacuated limb. Pressure measurements were made with a cathetometer whose scale was calibrated against a standard decimeter, ruled on glass, from the National Bureau of Standards. Pressure measurements could be duplicated to within ±0.005 cm.

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[11] The fumes from hot cottonseed oil have been found to be irritating and possibly harmful to the eyes and lungs. Care should therefore be exercised in the use of this substance.

[12] The outer surface of the click gauge was silver-plated. By means of lenses, light was made to converge at the mirror-like surface from which it was reflected to a screen. The reflected pattern varied with the position of the membrane in such a way as to facilitate greatly the use of the gauge. Measurements with the gauge used were reproducible to less than ±0.005 cm.

Corrections applied to all recorded data

Corrections were made to take account of the following items: (1) the thermal expansion of the Pyrex glass reaction vessel (the coefficient of expansion given in I.C.T.[13] was used), (2) the exposed stem of the thermometer (stem correction), (3) the almost negligible amount of nitric oxide present in the side arm when it was sealed off, (4) the quite small effect on the pressure caused by changes in temperature of the air in the unevacuated limb of the manometer during measurements, (5) the height of the menisci[14] and the temperature of the mercury in the manometer, and (6) the acceleration caused by gravity.[15]

At Pasadena $g = 979.57$ cm/sec.^{2}. The standard is $g = 980.67$ cm/sec.^{2}. Accordingly all pressure measurements recorded in the tables are in international centimeters of mercury[16] at $0°$.

In addition to these corrections, correction for the room temperature dead space (obnoxious volume) in the click gauge was also made. To do this it was assumed that the dead space contained only nitrosyl chloride and nitric oxide or chlorine depending on which of these was present in excess. This assumption is justified

[13] *International Critical Tables* (1929) Vol. II, p. 93.
[14] *International Critical Tables* (1929) Vol. I, p. 73.
[15] *International Critical Tables* (1929) Vol. I, p. 68.
[16] *International Critical Tables* (1929) Vol. I, p. 69.

for correction purposes since at room temperature only some 0.5 percent of the nitrosyl chloride at atmospheric pressure is dissociated. If, in the dead space, $(N°_{NO})_2$ is the number of moles of NO plus the number of moles of NOCl, and $(N°_{Cl_2})_2$ is the number of moles of Cl_2 plus half the number of moles of NOCl, then it is easy to show that with excess NO

$$(N°_{NO})_2 = PV_2/RT_2 \qquad (2)$$

with excess Cl_2

$$(N°_{NO})_2 = PV_2 2A/RT_2(A+2) \qquad (3)$$
$$A = (N°_{NO})_2/(N°_{Cl_2})_2,$$

where V_2 is the volume (2.3 ml) of the dead space, T_2 its temperature, and P the pressure. At each temperature the quantities $(N°_{NO})_2$ and $(N°_{Cl_2})_2$ are subtracted from the initial amounts of nitric oxide and chlorine respectively placed in the reaction vessel.

RESULTS OF THE EQUILIBRIUM MEASUREMENTS

Three separate fillings of the reaction flask were made, one with excess nitric oxide, one with excess chlorine and one with equivalent amounts. The initial amounts and pressures are presented in Table I. In Table II are given the observed equilibrium pressures, P, in international cm of Hg at $0°$, and the values of log K'_{cm} and log K_{cm}. K' was calculated from the following relation

TABLE II. *Results of equilibrium measurements.* $0°C = 273.10°K$, $K = P^2_{NO}P_{Cl_2}/P^2_{NOCl}$.

°K	RUN III			RUN IV			RUN V		
	P^*	$-\log_{10} K'_{cm}$**	$-\log_{10} K_{cm}$†	P	$-\log_{10} K'_{cm}$	$-\log_{10} K_{cm}$	P	$-\log_{10} K'$	$-\log K$
372.38	52.49	a	2.538	—	—	—	—	—	—
372.67	—	a	—	46.64	3.094	2.569	49.03	2.850	2.586
381.52	53.83	—	2.383	—	—	—	—	—	—
382.50	—	—	—	48.00	2.654	2.306	50.56	2.509	2.312
392.31	55.50	2.473	2.080	49.38	2.309	2.062	52.16	2.181	2.032
402.11	57.06	2.054	1.837	50.82	1.990	1.812	53.78	1.916	1.795
411.86	—	—	—	52.31	1.695	1.564	55.45	1.656	1.558
412.17	58.80	1.687	1.549	—	—	—	—	—	—
422.62	60.67	1.400	1.299	54.03	1.395	1.302	57.39	1.377	1.299
432.50	62.50	1.166	1.088	55.59	1.190	1.114	59.22	1.152	1.087
442.34	64.42	0.9358	0.8749	57.27	0.9611	0.9011	61.09	0.9362	0.8838
452.13	66.39	0.7275	0.6785	58.99	0.7506	0.7022	63.04	0.7265	0.6828
461.93	68.44	0.5323	0.4933	60.78	0.5538	0.5139	65.03	0.5364	0.4986
471.71	—	—	—	62.61	0.3713	0.3390	67.08	0.3551	0.3232
481.46	—	—	—	—	—	—	69.19	0.1767	0.1486
491.24	—	—	—	—	—	—	71.35	0.0120	−0.0122

* P = Equilibrium pressures in Int. cm Hg at $0°$.
** $\log_{10} K'_{cm}$ refers to actual gases.
† $\log_{10} K_{cm}$ refers to perfect gases.
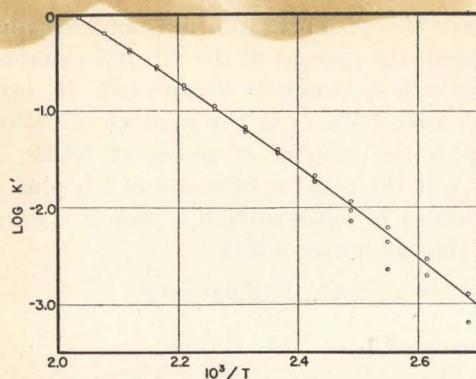a The values of $\log_{10} K'_{cm}$ are imaginary.

FIG. 2. Plot of log K' (assuming all gases perfect) against $1/T$.

FIG. 3. Plot of log K (corrected for gas imperfections) against $1/T$. The solid line was plotted from Eq. (12). Each circle represents one or more experimental values.

derived from the perfect gas laws.

$$K'_{cm} = (P^\circ_{NO} - 2\Delta P)^2 (P^\circ_{Cl_2} - \Delta P)/4\Delta P^2, \quad (4)$$

where P°_{NO} is the pressure of nitric oxide which would have existed at the temperature in question if no reaction had taken place, $P^\circ_{Cl_2}$ is the corresponding pressure of chlorine, and $\Delta P = P^\circ_{NO} + P^\circ_{Cl_2} - P$. The value of the gas constant used was $R = 6236.6$ ml cm/mole deg. and it was calculated from the I.C.T.[17] value $R = 82.06$ ml atmos./mole deg. Inasmuch as the gases involved are not perfect, additional experiments, to be described below, were made to determine the extent of the imperfections, and the results were used in arriving at $\log K$. K refers, therefore, to perfect gases.

At the higher temperatures the values of K' differ from the mean by ± 3 percent or less. This agreement can be considered as excellent. At the lower temperatures, and when one of the reactants is in excess, considerable difference in the values of K' is to be noted. Most of this difference arises from the fact that considerable errors in P_{Cl_2} or P_{NO}, especially when these are small, result from their calculation as differences in large pressures.

If the gases present at the larger pressures were perfect, the errors in P_{NO} or P_{Cl_2} would correspond only to the experimental error, but since the partial pressure of a gas present at a relatively high pressure as calculated from the perfect gas laws is not equal to its true pressure, it follows that a small pressure found by taking the difference between two large pressures will
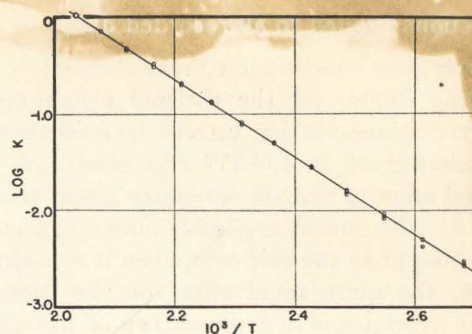
be in error by an amount much greater than that of the measurements. The main effect of the corrections for gas imperfection is that on the values of P_{Cl_2} and P_{NO}. At *low temperatures* the values of K' are very sensitive to the corrections and to errors in the measurements; the corresponding values of K are less sensitive since the effect of the corrections for gas imperfections is to make the small uncorrected pressures larger.

For the purposes of thermodynamics the fugacities of imperfect gases must be used in evaluating the equilibrium constants. In the present case it was found, as might be expected, that K_f, $K_{p(\text{real})}$ and $K_{p(\text{ideal})}$ differed but little. Thus at 422.6°C the difference is less than 0.5 percent, well within the allowed error. The correction of the thermodynamic quantities to the ideal gas state is also less than the small experimental errors in these quantities. Accordingly we can consider K, which was calculated using corrected pressures, as referring to the ideal gases. In Fig. 2 is shown a plot of $\log_{10} K'$ against $1/T$ and in Fig. 3 the corresponding plot for $\log_{10} K$, where K refers to perfect gases. It will be noted in the latter figure the points for the three runs show but little scattering over the whole temperature range investigated. At 471.74° Dixon's value for K' differs from that in the table by about 7 percent.

DETERMINATION OF THE GAS IMPERFECTIONS

The materials and experimental procedure were the same as those in the equilibrium measurements. An excess of nitric oxide was always added to repress the dissociation of the nitrosyl chloride. Over the temperature range 0°

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[17] *International Critical Tables* (1929) Vol. I, p. 18.

to 100° the pressures of mixtures of accurately known amounts of nitric oxide and chlorine were measured. In Table III are shown the initial amounts and pressures of chlorine and nitric oxide. Table IV contains the observed temperatures and pressures, as well as ΔP the difference between the observed pressure corrected for the imperfection of nitric oxide, and the pressure calculated for a mixture of perfect gases. Nitric oxide alone shows but little gas imperfection,[7] and it proved convenient to take this into account in arriving at the values of ΔP. Corrections were also made for the small equilibrium pressure of chlorine present, about 0.01 cm or less.

The equation of state of a pure imperfect gas over a limited range of temperatures and pressures can be taken as

$$P - NRT/V = NBP/V, \qquad (5)$$

where B is the second virial coefficient and is a function of the temperature. In the correction term on the right P may, to a good approximation, be replaced by NRT/V so that

$$P - NRT/V = BN^2RT/V^2 = B\bar{N}^2RT, \qquad (6)$$

where $\bar{N}$ is the number of moles per unit volume. For a mixture of n imperfect gases $\bar{N} = \bar{N}_1 + \bar{N}_2 + \cdots \bar{N}_n$. It will be assumed that B is a function of $\bar{N}_1, \bar{N}_2, \cdots \bar{N}_n$ such that the correction term $C = B\bar{N}^2RT$ will be given by

$$C_{1,2 \ldots n} = RT \sum_i^n \sum_j^n B_{ij} \bar{N}_i \bar{N}_j. \qquad (7)$$

B_{ij} is a measure of the interaction between the i and j molecules, and when $i = j$ B_{ij} is the second virial coefficient for the pure gas j. B_{ij} will be assumed, as seems likely, to be a function of B_{ii} and B_{jj} of such a kind that B_{ij} will be the mean of B_{ii} and B_{jj}. Of the various kinds of means, $B_{ij} = (B_{ii}B_{jj})^{\frac{1}{2}}$ seems, for physical reasons, less acceptable than $B_{ij} = (B_{ii}+B_{jj})/2$, since in the former case B_{ij} becomes vanishingly small when one of the gases is nearly perfect. The molecules of a gas which, by itself, is nearly perfect may well show appreciable interaction with the molecules of an imperfect gas. Accordingly, the final expression for $C_{1, 2 \ldots n}$ becomes, on dropping superfluous subscripts,

$$C_{1, 2 \ldots n} = \frac{RT}{2} \sum_i^n \sum_i^n (B_i + B_j) \bar{N}_i \bar{N}_j. \qquad (8)$$

Johnston and Weimer[7] have studied the imperfections of nitric oxide and Eucken and Hoffman[18] have made a similar study of chlorine. Nitric oxide shows comparatively little imperfection in the temperature range of interest, B_{NO} being about 10 percent of B_{Cl_2} or B_{NOCl}. For this reason the small imperfections of nitric oxide have already been taken into consideration in the calculation of ΔP from the experimental data.

Since B_{NO} is small and $B_{NO, NOCl} = (B_{NO} + B_{NOCl})/2$, $B_{NOCl} = 2B_{NO, NOCl}$ to a good approximation. In Table V are presented the values of $-B_{NOCl}$ for even temperatures calculated from smooth curve values of ΔP under the assumptions

TABLE IV. *Results of the experiments to determine gas imperfections.*

	RUN II		RUN IV	
°K	P. INT. cm Hg, 0°	ΔP cm	P. INT. cm Hg, 0°	ΔP cm
372.67	66.76	0.25	74.10	0.30
348.04	62.32	.28	69.17	.34
323.09	57.87	.27	64.20	.35
298.12	53.34	.32	59.20	.38
276.03	49.35	.35	54.73	.45

TABLE V. *The second virial coefficients of nitrosyl chloride.*

	$-B_{NOCl}$ IN cm³/MOLE			
t°C	RUN I	RUN II	MEAN	$-B_{Cl_2}$
100	202	191	196	135
75	224	212	218	169
50	260	245	253	215
25	314	300	307	274
0	398	380	389	343

TABLE III. *Initial amounts and pressures of chlorine and nitric oxide.*

VOL. SIDE ARM 19.6 ml IN RUN II; 21.4 ml IN RUN IV

RUN	WT. Cl₂ g	NITRIC OXIDE			APPROX. INITIAL MOLE RATIO NO/Cl₂
		PRESSURE INT. cm Hg AT 0°	TEMP. °C	VOL. ml	
II	0.6924	52.66	24.96	1071.6	3.11
IV	0.8169	58.96	27.96	1073.4	2.92

[18] Eucken and Hoffman, Zeits. f. physik. Chemie **B5**, 442 (1929).

set forth above. For comparison the values of $-B_{Cl_2}$ are also included in the table. The values of B_{NOCl} are of the same order of magnitude as those of B_{Cl_2} but larger, and this is to be expected since nitrosyl chloride has the higher boiling point, $-5.7°$. The error in B_{NOCl} is about 7 percent.

The values of B_{NOCl} were plotted and the plot extrapolated to 200° (where $B_{NOCl} = -116$ cm³/mole), and the extrapolated values, together with those for B_{Cl_2} and B_{NO}, were used in connection with Eq. (8) to arrive at the corrections applied to the results of equilibrium measurements. The corrections were made by a process of successive approximations, the second approximation usually sufficing. By far the greater part of the correction is due to the imperfection of nitrosyl chloride since this gas was always present at relatively high pressures.

THE THERMODYNAMIC QUANTITIES CALCULATED FROM THE EXPERIMENTAL RESULTS

When $\log K$ is plotted against $1/T$ the resulting curve is, within the limits of error (from less than ± 3 percent to ± 4 percent), a straight line. This fact indicates that ΔC_P for the reaction $2NOCl(g) = 2NO(g) + Cl_2(g)$ is small. Since ΔC_P could not be determined from the curvature of the $\log K$, $1/T$ curve, it was evaluated, as a function of T, from spectroscopic data. To this end use was made of published data on the heat capacities and entropies of nitric oxide[6] and chlorine[19] together with the vibrational frequencies (1888 cm⁻¹ for NO, 570 cm⁻¹ for Cl_2) of these molecules, to construct semi-empirical equations for C_P. The fundamental nondegenerate frequencies,[4] 633 cm⁻¹, 923 cm⁻¹ and 1832 cm⁻¹, of nitrosyl chloride were employed to arrive at an expression for C_P for this substance. The final result for ΔC_P is

$$2NOCl(g) = 2NO(g) + Cl_2(g),$$
$$\Delta C_P° = 8.237 - 0.021416T + 14.525$$
$$\times 10^{-6}T^2 \pm 0.01 \text{ cal./deg.} \quad (9)$$

This yields for ΔC_P, 3.14 cal./deg. at 298.1°K, 1.99 cal./deg. at 400°K and 1.16 cal./deg. at 500°K, and shows that, in agreement with experiments, ΔC_P is small.

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[19] Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).

From the slope of the $\log K$, $1/T$ curve a value of ΔH was determined. This when combined with ΔC_P yields the formula

$$\Delta H° = 16429 + 8.237T - 0.010708T^2$$
$$+ 4.8417 \times 10^{-6}T^3 \pm 180 \text{ cal.} \quad (10)$$

Finally the equations for $\Delta F°$, $\log_{10} K$ and ΔS may be established and are, respectively,

$$\Delta F° = 16429 - 18.967T \log_{10} T + 21.452T$$
$$+ 0.010708T^2 - 2.4208 \times 10^{-6}T^3 \pm 40 \text{ cal.}, \quad (11)$$

$$\log_{10} K_{cm} = -2.808 - 3591.0/T + 4.1457 \log_{10} T$$
$$- 0.0023406T + 0.52915 \times 10^{-6}T^2 \pm 0.02, \quad (12)$$

and

$$\Delta S° = -13.215 + 18.967 \log_{10} T - 0.021416T$$
$$+ 7.2625 \times 10^{-6}T^2 \pm 0.3 \text{ E.U.} \quad (13)$$

It is to be emphasized that spectroscopic data have been used here only in arriving at an expression for ΔC_P. In Fig. 3 the solid curve was plotted from the above equation for $\log_{10} K$; the circles indicate experimental values. The equation, within the limits of error, agrees with experiment throughout the temperature range investigated. Since ΔC_P is small, agreement would still result if this quantity were altered by as much as 50 percent.

From the above equations, and from the published values for the entropies at 25° of nitric oxide,[6] 50.35 cal./deg. and chlorine,[19] 53.31 cal./deg., the following thermodynamic quantities were calculated.

$$2NOCl(g) = 2NO(g) + Cl_2(g),$$
$$\Delta F°_{298} = 9,720 \pm 60 \text{ cal.},$$
$$\Delta H°_{298} = 18,060 \pm 200 \text{ cal.},$$
$$\Delta S°_{298} = 28.0 \pm 0.5 \text{ cal./deg.},$$
$$S°_{298}(NOCl) = 63.0 \pm 0.3 \text{ cal./deg.}$$

COMPARISON WITH SPECTROSCOPIC DATA

The entropies of nitric oxide and chlorine have been calculated from spectroscopic data, by Johnston and Chapman[6] and Giauque and Overstreet.[19] From their results the following semi-empirical equations were derived.

$$S°_{NO} = 7/2R \ln T + S_{1888} + 10.787 \text{ E.U.}, \quad (14)$$

$$S_{Cl_2} = 7/2R \ln T + S_{570} + 13.180 \text{ E.U.}, \quad (15)$$

where S_ω is the entropy associated with the vibrational frequency ω.

The moments of inertia of nitrosyl chloride, referred to principal axes, as calculated from Ketelarr and Palmer's[3] electron diffraction results are, $I_1 = 8.99 \times 10^{-40}$g cm^2, $I_2 = 146.8 \times 10^{-40}$ cm^2 and $I_3 = 155.8 \times 10^{-40}$g cm^2. The interatomic distances given by them are $N-O$ 1.14±0.02A, and $Cl-N$ 1.95±0.01A, and the bond angle $Cl-N-O$ is 116±2°. Bailey and Cassie's[4] infrared study led them to the conclusion that the fundamental frequencies of nitrosyl chloride were $\omega_1 = 1832$ cm^{-1}, $\omega_2 = 633$ cm^{-1} and $\omega_3 = 923$ cm^{-1}. ω_2 represents the bending frequency. From these data there was derived the relation

$$S°_{NOCl} = 4R \ln T + S_{633} + S_{923} + S_{1832} + 15.460 \text{ E.U.} \quad (16)$$

and finally the purely empirical relation

$$\Delta S(\text{spectr.}) = -9.605 + 18.967 \log_{10} T - 0.021416T + 7.2625 \times 10^{-6} T^2 \pm 0.01 \text{ E.U.} \quad (17)$$

The experimentally found relation is

$$\Delta S(\text{expt.}) = -13.215 + 18.967 \log_{10} T - 0.021416T + 7.2625 \times 10^{-6} T^2 \pm 0.3 \text{ E.U.} \quad (13)$$

A comparison of the spectroscopic and experimental values of ΔS shows immediately that

$$\Delta S(\text{spect.}) - \Delta S(\text{expt.}) = 3.61 \pm 0.3 \text{ E.U.} \quad (18)$$

that is, a discrepancy of 3.61±0.3 cal./deg. which is, within the limits of error, independent of the temperature. This is much larger than could possibly be accounted for by experimental error. It is smaller, but of the same order of magnitude as that calculated by Jahn[2] using Dixon's[1] measurements, namely 5.673 cal./deg.

There seems to be no escape from the assumption that the analyses of the spectroscopic data for nitric oxide and chlorine are correct. Accordingly, the discrepancy is caused by some uncertainty in the spectroscopic data for nitrosyl chloride, or its energy levels are degenerate as a result of some unknown factor. The former possibility only can be considered here. The discrepancy is such that the entropy of nitrosyl chloride calculated from spectroscopic data is too small. Consideration must be given to factors that would increase it by $\frac{1}{2}$ 3.6 = 1.8 E.U.

The interatomic distances of Ketelaar and Palmer cannot be increased greatly without making them improbably large. The $Cl-N$

distance of 1.95A is, according to these authors, already larger by 0.26A than that to be expected. A change in the bond angle from 116° to the improbably small value of 90° increases $S°_{NOCl}$ by only 0.3 E.U. Accordingly it does not seem likely that the discrepancy results from uncertainty in the size or shape of the molecule.

It is possible that not all of the frequencies reported by Bailey and Cassie are fundamentals. The frequency 1832 cm^{-1} is, as is to be expected, nearly equal to that found with nitric oxide, 1888 cm^{-1}, and hence is, in all probability, a fundamental. The following considerations indicate that the 923 cm^{-1} frequency is not a fundamental. Lechner[20] has derived formulas for the fundamental frequencies of unsymmetrical triatomic molecules as a function of the force constants for stretching and bending. The force constants for the $N=O$ and $N-Cl$ bonds may be evaluated from Badger's Rule[21] and were found to be $k_{12} = 15.0 \times 10^5$ and $k_{23} = 1.6 \times 10^5$ dynes/cm, respectively. Two of Lechner's relations take the following forms:

$$\omega_1^2 + \omega_2^2 + \omega_3^2 = 35.92 \times 10^5 + 6.01d, \quad (19)$$

$$\omega_1^2 \omega_2^2 \omega_3^2 = 346 \times 10^{10} d, \quad (20)$$

where d is the bending force constant and ω_1, ω_2, ω_3 are frequencies expressed in cm^{-1}. If the molecule were linear the terms ω_2^2 and $6.01d$ in the first equation would be absent. With $\omega_1 = 1832$ cm^{-1}, ω_3 becomes 490 cm^{-1}. The molecule is not linear but has a bond angle of 116°. The value of ω_3 will be somewhat different for the bent model but not greatly so; it seems reasonable then to select the observed frequency 633 cm^{-1} for ω_3. It is now possible to evaluate approximately the bending frequency ω_2 and the force constant d. $\omega_2(\text{calc.}) = 346$ cm^{-1}. $d = 0.46 \times 10^5$ dyne/cm. This value of ω_2 is considerably lower than the lowest observed frequencies, namely 633 cm^{-1} and 923 cm^{-1}. If it is assumed that the greater of these is a combination such that 923 = 633 + 290, then the fundamental frequencies for nitrosyl chloride become 1832, 290 and 633 cm^{-1}, respectively. Professor R. M. Badger has called our attention to the fact that further support for the assumption is provided by the low

[20] Lechner, Monatshefte für Chem. 61, 385 (1932).
[21] Badger, J. Chem. Phys. 2, 128 (1934); 3, 710 (1935).

bending frequency[22] of 397 cm^{-1} for $Cl-C\equiv N$, a linear molecule that is probably stiffer than $Cl-N=O$. The assumption of the low bending frequency leads to a much smaller discrepancy between theory and experiment, namely

$$\Delta S°\text{(spect.)} - \Delta S\text{(expt.)} = 0.40 \text{ E.U. at } 100°$$
$$= 0.10 \text{ E.U. at } 220°$$

and the largest of these values is only slightly greater than the average experimental error, ± 0.3 E.U. The effect of the lowered frequency on ΔC_P has been taken into account, and the effect on $\Delta H°$ and $\Delta F°$ is found to be less than the experimental error.

Another possible interpretation of the infra-red spectrum is that both the 923 cm^{-1} and 633 cm^{-1} bands are first harmonics. The fundamentals would then be 1832, 317 and 462 cm^{-1}, respectively. This interpretation would be in accord with the considerations based on Lechner's formulas. The discrepancy between the spectro-

scopic and experimental entropy changes is reduced to 0.30 cal./deg. at 220° and to 0.80 cal./deg. at 100°. This result is not as satisfactory as that obtained through the assumption that $923 = 633 + 290$ cm^{-1}.

The discrepancy reported by Jahn is to a large extent removed if the assumption of the lowered frequency is made. That it is not wholly removed may possibly be ascribed to the experimental errors in Dixon's results.

The possibility of finding some new and interesting kind of degeneracy should not, of course, be overlooked. Before ascribing the discrepancy to such a cause a further investigation of the infra-red spectrum of nitrosyl chloride should be made, or its heat capacity determined. Because of the intense red color of the substance it has not been found possible to obtain its Raman spectrum.[23] The tentatively predicted frequency of about 290 cm^{-1} falls in the infra-red region at 30–40μ.

[22] Sutherland, Proc. Roy. Soc. **A156**, 654 (1936).

[23] Dadieu and Kohlrausch, Physik. Zeits. **33**, 165 (1932).

The Diamagnetism of Gaseous Nitrosyl Chloride*

In a recent paper Jahn[1] suggested that nitrosyl chloride (NOCl) exists in a triplet normal state, perhaps with a low-lying singlet state, in order to explain the apparent excess entropy of $R \ln 3$ or $R \ln 4$ calculated from equilibrium measurements over that calculated from structural and spectroscopic information. This triplet ground state would lead to paramagnetism of the substance. Wilson[2] made magnetic measurements on liquid nitrosyl chloride and found it to be diamagnetic. There remains, however, the possibility that polymerization of the molecules in the liquid state might reduce the paramagnetism of the substance, as is the case with oxygen at sufficiently low temperatures. We have therefore carried out measurements on the gaseous compound.

The susceptibility was measured at 25° by the Gouy method, making comparison with oxygen as the substance of known paramagnetism ($\kappa = +0.142 \times 10^{-6}$ c.g.s.m. at 20°).[3] A glass tube of 19 mm diameter was separated into two compartments by a glass septum and equipped at either end for sealing off. This was suspended from the arm of an analytical balance, and the apparent change in weight (Δw in mg) of the tube was determined when the magnet was excited with two different currents. The absolute values of the magnetic fields obtained were 8080 and 9350 oersteds at 9.00 and 14.00 ampere readings. With both ends evacuated there were found for the corresponding readings $\Delta w = +0.10$ and 0.16 (average of at least two determinations); with the upper end evacuated and dried tank oxygen at 701 mm pressure at 25° in the lower end, $\Delta w = -8.29$ and -11.08; with the upper end evacuated and pure nitrosyl chloride at 790 mm pressure at 25° in

the lower end, $\Delta w = +0.11$ and 0.14. The probable error in the determination of Δw is of the order of ± 0.05 mg. The nitrosyl chloride was prepared from nitric oxide and chlorine which had been carefully purified for use in equilibrium measurements. A large excess of nitric oxide was allowed to react with the chlorine, and the nitrosyl chloride was then frozen out in the tube and pumped free from volatile impurities.

The predicted values of Δw for nitrosyl chloride in a $^3\Sigma$ state at the pressure and temperature of measurement are -9.3 and -12.5; the predicted values for equipartition between three $^3\Sigma$ and one $^1\Sigma$ states (quantum weight four) are -7.0 and -9.3; the predicted values for a singlet state (diamagnetic), taking into account the estimated molecular diamagnetism of -30×10^{-6}, are $+0.19$ and 0.28 respectively. Correction for an estimated dissociation of 0.5 percent[4] into chlorine and paramagnetic nitric oxide would lower the diamagnetic values to $+0.15$ and $+0.24$ respectively. The observed Δw values are in satisfactory agreement with this last prediction. We conclude therefore that nitrosyl chloride is diamagnetic and in a singlet state.

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      August 23, 1938.

[1] F. P. Jahn, J. Chem. Phys. 6, 335 (1938).
[2] E. B. Wilson, Jr., J. Am. Chem. Soc. 56, 747 (1934).
[3] International Critical Tables, VI, 354 (1929).
[4] Extrapolation of unpublished equilibrium data of C. M. Beeson and D. M. Yost.

The Thermodynamic Constants of Bromine Chloride.
The Equilibrium Reaction between Nitric Oxide, Bromine, Chlorine,
Nitrosyl Bromide and Chloride, and Bromine Chloride.

By Carrol M. Beeson and Don M. Yost

Introduction

The degree of dissociation of gaseous bromine chloride,
BrCl, at room temperature has been determined by several
investigators by light absorption methods, and the results are
in fair agreement. The use of Chemical methods for studying
the equilibrium has so far been restricted to studies at
rather high temperatures, namely 500 and 800 . In these
determinations, mixtures of fused chlorides and bromides, for
example the silver chloride-silver bromide pair, are in
equilibrium with gaseous chlorine, bromine and bromine chloride.
A knowledge of the activities of the component salts is necessary
in order to evaluate the partial pressures of the three gases.
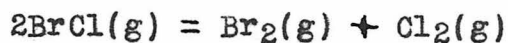The reversible gas reaction under consideration is

$$2BrCl(g) = Br_2(g) + Cl_2(g) \tag{1}$$
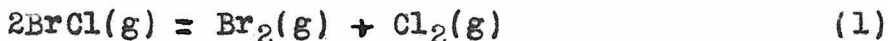
$$K_{BrCl} = P_{Br_2} P_{Cl_2} / P_{BrCl}^2 \tag{2}$$

The results of all former measurements of the equilibrium
constant of reaction (1) are summarized in Table I. The
weighted mean value of K at room temperature was obtained by
giving to each value a weight inversely proportional to the
stated error; the two widely different values of Jost were
omitted in calculating the mean. This method of estimating
the mean is not free from criticism, but it appears to be as
satisfactory as any in arriving at a value that is representative
of those obtained by all investigators.

Table I

Summary of Equilibrium Constants for the Reaction:

$$2BrCl(g) = Br_2(g) + Cl_2(g)$$

$$K_{BrCl} = P_{Br2} \, P_{Cl2} \, / \, P^2_{BrCl}$$

Date	Authors	Method	°C Temp.	K
1930	Gray and Style (1)	Light Absorbtion	Room	0.132, to 0.125
1931	Jost(2)	"	"	0.10 to 0.22
1933	Dickinson and Murdoch(3)	"	"	0.12 ± 0.01
1934	Vesper and Rollefson(4)	"	28°	0.107 ± 0.002
1935	Brauer and Victor(5)	"	Room	0.144 ± 0.003
1935	Jellinek and Schutza(6)	KCl(L), KBr(L) Br$_2$(g), Cl$_2$(g) BrCl(g) and other salt pairs	800°	0.12
1938	Schutza	AgCl(L), AgBr(L) Br$_2$(g), Cl$_2$(g), BrCl(g) also PbCl$_2$, PbBr$_2$(L) and other salt pairs	500° 800°	0.1325 0.140

Weighted Mean Value at Room Temperature K = 0.126

In the present paper are described the results of
equilibrium measurements on the gaseous system nitric oxide,
bromine, chlorine, nitrosyl bromide and chloride, and bromine
chloride in the temperature range from 372 to 492 K. The
reversible reactions taking place may be regarded as the
following:

$$2NOBr(g) = 2NO(g) + Br_2(g) \qquad -(3)-$$

$$2NOCl(g) = 2NO(g) + Cl_2(g) \qquad -(4)-$$

$$2BrCl(g) = Br_2(g) + Cl_2(g) \qquad -(1)-$$
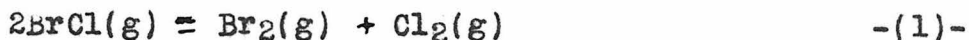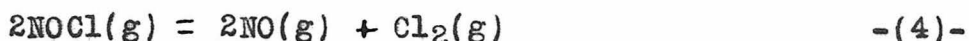
and measurements of the total pressure of the system and a
knowledge of its composition makes possible the calculation of
K_{BrCl}. The equilibrium constants, for reaction -(3)- were
determined by Blair, Brass and Yost[8], and are given, as a
function of the temperature, by the expression:

$$K_{NOBr} = P_{NO}^2 \, P_{Br2}/P_{NOBr}^2 \qquad -(5)-$$

$$\log_{10}K_{NOBr}(cm) = -9.325 - 1919/T + 6.750 \log_{10}T - 0.00407 \, T$$
$$+ 1.27 \; 10^{-6}T^2 \qquad -(6)-$$

The constants for reaction -(4)- were determined recently by
Beeson and Yost[9] and may be calculated from the relation:

$$K_{NOCl} = P_{NO}^2 \, P_{Cl_2}/P_{NOCl}^2 \qquad -(7)-$$

$$\log_{10}K_{NOCl}(cm) = -2.808 - 3591.0/T + 4.1457 \log_{10}T - 0.0023406 \, T$$
$$+ 0.52915 \; 10^{-6}T^2 \qquad -(8)-$$

In both cases the K(cm) are expressed in centimeters of
mercury at $0°$ and sea level, and they have been corrected for
gas imperfections. The experimental errors amount to ± 2 %
for K_{NOBr} and from ± 1% to ± 2% for K_{NOCl}.

Preparation of Materials and Experimental Methods

Materials: The nitric oxide and chlorine were prepared with
great care and were portions of the same materials used in
the investigation of nitrosyl chloride[9]. The chlorine
contained less than 0.1% of hydrogen chloride, and the nitric
oxide was of high purity and free from other oxides of nitrogen.
Bromine was prepared by treating a saturated solution of
twice recrystallized potassium bromate and bromide with
chemically pure sulfuric acid. The bromine was distilled
from this mixture and then dried over and repeatedly distilled
from specially purified anhydrous calcium bromide, fresh
portions of the latter being used for each distillation.

Only the middle fraction of the bromine was used in the equilibrium measurements. Both the bromine and chlorine were condensed and sealed in glass capsules equipped with easily breakable tips.

Experimental Procedure: The nitric oxide, bromine, and chlorine were introduced into a one liter evacuated Pyrex glass flask, the manner of filling differing but little from that described in the papers on nitrosyl chloride and bromide(8,9). At no time did the chlorine and bromine come in contact with stopcock grease or other organic matter: glass enclosed magnetic devices were used to break the capsules containing these substances, and the pressures were measured by means of a glass click gauge. The thermostated mercury manometer had an inside diameter of 2.15 cm., and the heights of its arms were read to 0.005 cm. with a cathetometer whose scale had been calibrated against a standard decimeter, ruled on glass, from the National Bureau of Standards. The reaction flask was immersed in a hydrogenated cottonseed oil filled thermostat whose temperature was kept constant to $\pm 0.1°$. Temperatures were measured to $0.05°$ with mercury thermometers which were calibrated periodically against thermometers from the National Bureau of Standards.

Corrections: Corrections were made to take account of the thermal expansion of the Pyrex glass reaction vessel(10), the exposed part of the thermometer, the height of the menisci and the temperature of the mercury in the manometer(11), the acceleration due to gravity (at Pasadena g 979.57 cm/sec^2; the standard is g 980.67 cm/sec^2.), the obnoxious volume, and gas imperfections. Other minor corrections were made to take account of the small temperature changes in the air filled side of the manometer and the small amount of nitric oxide present in a side arm when it was sealed off.

The most important single correction involving the nature of the reaction vessel was that due to the small obnoxious volume (dead space) of the click gauge and its connecting tube. This correction was made on the assumption that equilibrium was established in the dead space corresponding

to its temperature, namely that of the room.

Corrections were made for the effect of gas imperfections in the manner described below. The principal effect of these corrections is on the magnitudes of those partial pressures which are small. This is because small partial pressures are obtained as differences in larger pressures, and if the gases present at the larger pressures are imperfect, the differences in their pressures can be in considerable error if corrections are not made.

Results of the Equilibrium Measurements

In order to calculate the equilibrium constants for the dissociation of bromine chloride, the following independent relations were derived from the perfect gas laws:

$$K_1 = P_{NO}^2\, P_{Cl_2}/P_{NOCl}^2, \quad K_2 = P_{NO}^2\, P_{Br_2}/P_{NOBr}^2, \quad K_{BrCl} = P_{Br_2}\, P_{Cl_2}/P_{BrCl}^2$$

$$P_{NO} = P_{NO}^\circ - P_{NOCl} - P_{NOBr} = P_{NO}^\circ - 2\Delta P$$

$$P_{Cl_2} = P_{Cl_2}^\circ - \tfrac{1}{2}P_{NOCl} - \tfrac{1}{2}P_{BrCl}$$

$$P_{Br_2} = P_{Br_2}^\circ - \tfrac{1}{2}P_{NOBr} - \tfrac{1}{2}P_{BrCl}$$

where P_{NO}°, $P_{Cl_2}^\circ$ and $P_{Br_2}^\circ$ are the partial pressures that would obtain if no reaction took place, the other Ps are actual partial pressures, and ΔP is the difference between the observed pressure, P, and the pressure calculated on the assumption of no reaction, $\Delta P = P_{NO}^\circ + P_{Cl_2}^\circ + P_{Br_2}^\circ - P$. These equations, when solved under the assumption that K_1 is small (about 0.1%) compared to K_2 yield:

$$P_{NOBr} = \left\{K_2(P_{Br_2}^\circ + P - P_{Cl_2}^\circ) + P_{NO}^2/4 + 4K_1 K_2 \Delta P^2/P_{NO}^2\right\}^{\frac{1}{2}} P_{NO}/K_2$$
$$- P_{NO}^2/2K_2$$

$$P_{NOCl} = 2\Delta P - P_{NOBr}$$

$$P_{BrCl} = P - P_{NO} - P_{NOBr} - P_{NOCl} - P_{Cl_2} - P_{Br_2}$$

and these, together with the other more obvious relations, permit the calculation of K_{BrCl}. The value used for the gas constant R was 6236.6 ml.cm./Deg.mol. and it was calculated from the International Critical Tables' value of 82.06 ml. atm./Deg.mol.(12).

It was soon found that equilibrium was established rapidly at all temperatures investigated. This fact is of interest in view of the fact that nitric oxide reacts slowly with chlorine or bromine alone; evidently the reaction mechanism in the mixture involves rapid reactions not possible when only one halogen is present with nitric oxide. This same phenomenon was observed by McMorris and Yost(13) in the investigation of gaseous mixtures of nitric oxide, chlorine, iodene and iodine monochloride.

Three separate fillings of the reaction vessel were made with the varying initial amounts of reactants shown in Table II. In Table III are presented the equilibrium pressures P for the three fillings together with the values of the equilibrium constants $K = P_{Br_2}\, P_{Cl_2}/P_{BrCl}^2$. The constants K^1 were calculated without taking into account gas imperfections; the constants K were obtained after correcting for the imperfections. All pressures are expressed in international centimeters of mercury at $0°$.

It was found not difficult to adjust the temperature of the thermostat to a predetermined value, and this made it possible to determine equilibrium pressures at the same temperature for all runs. Measurements were made both while ascending and descending the temperature scale, and the two final values of P for any temperature obtained by approaching equilibrium from two directions, did not differ by more than 0.02 cm.

Discussion: The values of K^1 listed in Table III were calculated under the assumption that all gases obeyed the perfect gas laws. A comparison of the K^1 shows that they are in good agreement at the higher temperatures for all three runs but at lower temperatures the values for Run II are considerably greater than those for the other runs. This deviation is due to the circumstance that the smaller partial pressures of some of the components in Run II are more sensitive to gas imperfections than is the case with Runs I and III.

In making the corrections for gas imperfections it must be borne in mind that it is not possible at this time to make exact estimates of the second virial coefficients for the individual gases present in the equilibrium mixtures, and, moreover, our knowledge of the interactions between the molecules of unlike gases is so incomplete that only crude estimates of them are possible. In the investigation of nitrosyl chloride(9) it was possible to evaluate the magnitude of the imperfections in a fairly satisfactory manner. In the present case, since the relative amounts of nitric oxide, chlorine, and nitrosyl chloride were approximately the same as those in the investigation of nitrosyl chloride, and since the imperfections of nitrosyl bromide, bromine, and bromine chloride will doubtless be of the same order of magnitude as those of nitrosyl chloride and chlorine, it was decided to assume that the corrections would be equal to the same percentages of the total pressures as were found in the nitrosyl chloride equilibrium measurements. These percentages varied from 0.39% at 100° to 0.17% at 220°.

The effect of applying the gas imperfection corrections is to reduce the abnormally high values of K^1 for Run II at the lower temperatures to values of K that are more nearly equal for the three runs. This indicates that the order of magnitude and nature of the correction has been correctly estimated. That the magnitudes and manner of making the corrections are not exactly correct is shown by the fact that, at the lower temperatures, the values of K are not sufficiently constant. Another factor causing the lack of constancy is the greater effect of experimental errors in the lower temperature range.

At 432° K and above, the values of K for each run are nearly constant; they do show a tendency to increase slightly with temperature, but the increase is no greater than the variation from run to run. Inasmuch as the value of ΔH for

Table II

Initial Amounts of Reactants

Volume of reaction vessel = 1049.7 ml. at 20°

Volume of dead space = 2.3 ml. at 20°

Run	Wt. Br_2 grams	Wt. Cl_2 grams	Nitric Oxide Pressure Int. cm. Hg at 0°	Temp. °C	Vol. ml*	Approx. mol. Ratios Br_2	Cl_2	NO
I	0.7491	0.6544	24.18	23.97	1088.2	1	2.0	3.0
II	0.7737	0.7487	25.01	22.25	1088.4	1	2.2	3.1
III	0.9938	0.5358	27.26	22.20	1088.9	1	1.2	2.6

* This is volume of NO before it was condensed and the side arm sealed off.

Table III

Results of the Equilibrium Measurements

$$0^{\circ}\ C = 273.1\ ^{\circ}K$$

		Run I			Run II			Run III	
Temp. $^{\circ}K$	P Cm.	K^1	K	P Cm.	K^1	K	P Cm.	K^1	K
372.67	46.92	0.22	0.07	50.61	4.9	0.10	49.86	0.30	0.14
382.50	48.34	.19	.07	52.09	1.5	.13	51.50	.28	.15
392.31	49.78	.19	.08	53.63	0.63	.13	53.17	.29	.17
402.11	51.30	.18	.09	55.20	.46	.13	54.89	.24	.16
411.86	52.84	.18	.10	56.81	.32	.12	56.64	.23	.16
422.62	54.61	.16	.10	58.68	.22	.10	58.67	.21	.15
432.50	56.27	.16	.11	60.42	.24	.13	60.55	.20	.15
442.34	57.99	.16	.11	62.22	.22	.13	62.43	.20	.15
452.13	59.74	.16	.12	64.05	.21	.14	64.36	.20	.16
461.93	61.51	.17	.13	65.93	.22	.15	66.32	.20	.16
471.71	63.33	.17	.13	67.84	.22	.16	68.27	.19	.16
481.46	65.18	.17	.14	69.80	.22	.17	70.29	.20	.18
491.24	67.08	.18	.15	71.81	.22	.18	72.33	.21	.19

Mean of all K's for temperatures above 432° K is:

$$K(Mean) = 0.148 \pm 0.011$$

corresponding to a mean temperature of 462° K.

the formation of bromine chloride from bromine and chlorine is certainly small, it is believed that the variations of K with temperature and from run to run are due principally to our inability to evaluate correctly the effect of gas imperfections and to experimental error.

The Thermodynamic and Molecular Constants of Bromine Chloride

The mean of the twenty one values of K between $432°$ and $492°$ K is K = 0.148 ± 0.011 and is probably a reliable one for the mean temperature of $462°$ K. The weighted mean of the values of K at room temperature ($301°$) is 0.126. On the very reasonable assumption that ΔH is effectively constant between $301°$ K and $462°$ K, there results:

$$Br_2(g) + Cl_2(g) = 2BrCl(g) \qquad -(9)-$$
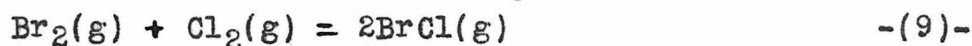
ΔH = -270 cal. ΔF_{298} = -1230 cal. ΔS_{298} = 3.22 cal./Deg.-(10)-

$$\Delta F_T = -270 - 3.22T$$

This free energy equation yields for $1100°$ K, the upper temperature employed by Schutza(6), K = $P_{Br2} P_{Cl2}/P_{BrCl}^2$ = 0.18, a value considerably higher than that reported, namely 0.140. It might be supposed that H is much smaller than that calculated here, and that in addition the mean room temperature value of K = 0.126 has not been correctly estimated. In this event one would expect to obtain nearly the same value of K at all temperatures in the range investigated, namely 0.14. Some of the results reported for room temperatures would be in accord with this supposition (Brauer and Victor(5)), while others would not (Vesper and Rollefson(4)).

An independent estimate of ΔH for reaction-(9)- was obtained by Blair and Yost(14), who measured the heat of the reaction:

$$\tfrac{1}{2}Br_2(in\ CCl_4) + \tfrac{1}{2}Cl_2(in\ CCl_4) = BrCl(in\ CCl_4)$$
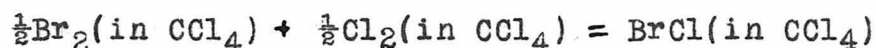
$$\Delta H_{298} = -378\ cal.$$

and, since the values of ΔH for the formation of ICl(g) and IBr(g) from the elements in the gaseous state are about 20 % less than those found for the same reactions in carbon tetrachloride solutions, they suggested that ΔH for reaction -(9)- would be -600 cal. When our value of K = 0.148 at $462°$ K is combined with that of Vesper and Rollefson, K = 0.107 at $301°$ K, the value calculated for ΔH is -570 cal. This in turn yields:

$$Br_2(g) \; \blacklozenge \; Cl_2(g) = 2BrCl(g) \qquad\qquad -(9)-$$
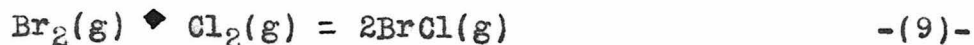
$$\Delta F^{\circ}_{301} = -1330 \text{ cal.} \quad \Delta H = -560 \text{ cal.} \quad \Delta S_{301} = 2.56 \text{ cal. Deg.}$$

$$\Delta F_T = -560 - 2.56T \qquad\qquad -(11)-$$

In order to decide between these three alternatives it is necessary to make use of the spectroscopic data for bromine, chlorine and bromine chloride.

Spectroscopic Data: The interatomic distances for Br_2 and Cl_2 are 2.28 A(15) and 1.988 A(16) respectively, and their mean, 2.13 A, will be assumed to be the interatomic distance for BrCl. This assumption conforms with the principle of the additivity of covalent radii(17). The vibrational frequency of bromine chloride was determined by Cordes and Sponer(18) and is 430 cm^{-1}. The internuclear distance, the frequency and the values of K_{BrCl} lead to the following values for ΔH°_0 the heat content change at T = 0, ΔS, and ΔH for the reaction under consideration. The necessary data for bromine was taken from the paper by Gordon and Barnes(19) and that for chlorine from Giauque and Overstreet (20).

Table IV

Thermodynamic Constants from Spectroscopic and Equilibrium Data

$$Br_2(g) + Cl_2(g) = 2BrCl(g)$$
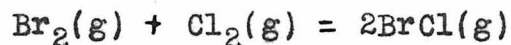
| $T^{\circ}K$	301°	462°
ΔS(spect.) Cal./Deg.	2.82	2.84
ΔH°_0 Cal.	-350^{a} -470^{b}	-434^{c}
ΔH Cal.	-366^{a} -486^{b}	-443^{c}

a, $K_{BrCl} = 0.126$ b, $K_{BrCl} = 0.107$ c, $K_{BrCl} = 0.148$

It is evident that $\Delta H_{\circ}^{\circ}$ is more nearly constant when Vesper and Rollefson's room temperature value of K_{BrCl} is assumed. Accordingly the free energy equation -(11)- is the more acceptable than -(10)-. Inasmuch as the ΔS calculated from spectroscopic data is probably more reliable than that derived from equilibrium data alone, the following free energy equation can be regarded as best representing the data.

$$Br_2(g) + Cl_2(g) = 2BrCl(g)$$
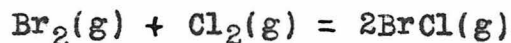
$$\Delta F_T = -465 - 2.83T$$

We are indebted to Dr. D. P. Stevenson for making some of the calculations in this section.

Summary

Careful measurements on the gas phase equilibrium between nitric oxide, bromine, chlorine, nitrosyl chloride and bromide, and bromine chloride have been made in the temperature range $372°$ K to $492°$ K. From the results, after an approximate correction for gas imperfections, the values of

$$K = P_{Br_2} P_{Cl_2}/P_{BrCl}^2$$

were calculated. The mean value of K at $462°$ K is 0.148 $\pm$ 0.011.

This value of K was combined with the values obtained at room temperature by other investigators to calculate the heat content change ΔH attending the formation of two mols of bromine chloride. Three possible values were obtained, zero, -270 and -560 cal. depending on the room temperature value of K_{BrCl} selected. Spectroscopic data were employed to show that the probable value of ΔH is -465 cal. The most acceptable free energy equation for the reaction $Br_2(g) + Cl_2(g) = 2BrCl(g)$, is $\Delta F_T = -465 - 2.83T$.

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Propositions to be Defended by Carrol M. Beeson.

1. Maxwell's electromagnetic equation Curl $E = -(1/c)\partial B/\partial t$ is not complete.

2. The discrepancy in ΔS° for the reaction

$$2\ NOCl(g) = 2\ NO(g) + Cl_2(g),$$
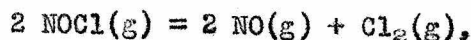
as revealed by Beeson and Yost (1), is due to one or more of the following causes:

    1. The vibrational frequencies of nitrosyl chloride, reported by Bailey and Cassie (2) are not all fundamentals.

    2. The entropy of nitric oxide, as calculated from spectroscopic data (3), is too large by $(1/2)$ R ln 2 E. U.

    3. The energy levels of nitrosyl chloride are degenerate as a result of some unknown cause.

3. A good approximate correction for the imperfections of gaseous mixtures is expressed by the relation

$$C_{1,\text{---}n}(total) = RT\ \left[B_1 N_1^2 + B_2 N_2^2 + \text{----} + B_n N_n^2 + (B_1 + B_2)N_1 N_2 \right.$$
$$\left. + \text{----} + (B_1 + B_n)N_1 N_n + \text{----} + (B_2 + B_n)N_2 N_n \right],$$

where $C_{1,\text{---}n}(total)$ represents the total deviation of the mixture from ideality, B_n represents the second virial coefficient for the pure gas n, and N_n expresses the number of mols per unit volume of component n in the gaseous mixture.

4. T. S. Moore's (4) method for the determination of the degree of hydration of amines is valid.

5. The thermodynamic constants of gases can be obtained most accurately by combining a small number of accurate equilibrium measurements with calculations from reasonably accurate spectroscopic data.

6. A necessary and sufficient condition that a gaseous solution obey the fugacity rule, $f_k = x_k f_k^\circ$, (where f_k is the fugacity of component k in

the solution, x_k is it's mol fraction, and f_k^o is the fugacity of the pure gaseous component at the temperature and pressure which obtain in the solution), is that the volumes of the constituents be additive.

7. Unimolecular homogeneous gaseous reactions have been successfully treated by recently developed theory.

8. Bodenstein's (5) explanation of the negative temperature coefficient for the rate of the reaction

$$2 \; NO(g) + O_2(g) = 2 \; NO_2(g),$$
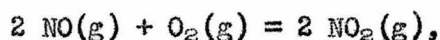
is sound.

9. The vibrational frequency of bromine chloride is probably about 446 cm^{-1}.

10. The chemistry laboratories of the California Institute of Technology should be equipped with movable hoods.

11. A reasonable mechanism which explains the rapid formation of bromine chloride in the presence of nitric oxide can be given.

12. Atomic nuclei are composed of neutrons and protons.

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