

the sulfuric acid-malic acid complex. The inhibitor thus decreases the concentration of the complex and thereby slows down the reaction.

The explanation for the maximum appears to be the same as for the other acids mentioned;² *i. e.*, there exists an equilibrium, $\text{H}_2\text{SO}_4 \rightleftharpoons \text{SO}_3 + \text{H}_2\text{O}$. As water is removed the velocity of decomposition is accelerated until a point is reached where the inhibiting effect of the increased concentration of sulfur trioxide more than offsets the accelerating effect due to the removal of water. The maximum in the velocity of decomposition of malic acid came at a molality of water of 0.024 and 0.030 at 35 and 45°, respectively, as compared to citric acid which exhibits a maximum at molalities of water of 0.10, 0.14, 0.20 at 15, 25 and 35°, respectively.⁴ The position of the maximum and the slope of the curve on either side of the maximum in both cases are evidence for the correctness of Wiig's explanation. In each case sulfur trioxide is a stronger inhibitor than water (as evidenced by the steeper slope of the curve in the sulfur trioxide region); hence, the maximum appears at a small concentration of water. The relative effect is not so pronounced in the case of malic acid as in citric acid, so that the maximum falls nearer to zero concentration of water. One would expect from this theory, if sulfur trioxide and water should have the

same inhibiting power in the decomposition of some compound, the curve for the velocity of decomposition would be symmetrical and exhibit a maximum at 100% H_2SO_4 .

The sharp flattening out of the curve after a concentration of about 2% sulfur trioxide has been reached is interesting. More than enough sulfur trioxide is then present to form a molecular compound with all of the malic acid or malic acid-sulfuric acid complex present; hence, the velocity measured from this point on may be that of the disintegration of this new complex.

The author wishes gratefully to express his appreciation to Dr. Edwin O. Wiig, under whose direction this work has been done, for his sincere and friendly interest in the completion of it.

Summary

The decomposition of malic acid by sulfuric acid has been found to proceed in the same manner as formic, oxalic and citric acids.

A maximum in the rate of decomposition has been found, the rate increasing up to a certain point as water was removed, then decreasing. The location of this maximum, which has been overlooked in a previous investigation, brings malic acid into agreement with the theory for inhibition in the decomposition of these acids.

ROCHESTER, N. Y.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Equilibrium in the Reaction $\text{Cl}_2 + \text{Br}_2 = 2\text{BrCl}$

BY HAROLD G. VESPER AND G. K. ROLLEFSON

The existence of bromine chloride has been a subject of dispute for many years. Early investigators¹ recorded the formation of a yellow or red-brown liquid when chlorine was passed into bromine in a freezing mixture, or bromine into liquid chlorine, and assumed the liquid to contain bromine chloride. That this was other than a solution of bromine and chlorine was questioned² on the basis of the small heat developed in the process, and from studies of the freezing point- and boiling point-composition curves. However, Andrews and Carlton³ noted a marked contraction

in volume upon mixing liquid bromine and liquid chlorine, and workers⁴ in the field of organic chemistry have for some time reported that mixtures of bromine and chlorine in addition reactions give bromochloro products, as if the substance adding were bromine chloride.

Physicochemical evidence for the formation of the compound BrCl on mixing Br_2 and Cl_2 in carbon tetrachloride solution was furnished by Barratt and Stein⁵ and by Gillam and Morton.⁶ It was found that the absorption of light by the mixtures, in the visible region, was markedly less

(1) (a) Balard, *Ann. chim. phys.*, [2] **32**, 337 (1826); (b) Schönbein, *J. prakt. Chem.*, [1] **88**, 483 (1863); (c) Bornemann, *Ann.*, **189**, 184 (1877); (d) Thomas and Dupois, *Compt. rend.*, **143**, 282 (1906).

(2) (a) Berthelot, *Compt. rend.*, **94**, 1619 (1882); (b) Lebeau, *ibid.*, **143**, 589 (1906); (c) Karsten, *Z. anorg. Chem.*, **53**, 365 (1907).

(3) Andrews and Carlton, *THIS JOURNAL*, **29**, 688 (1907).

(4) (a) Simpson, *Proc. Roy. Soc. (London)*, **A27**, 118, 424 (1879); (b) James, *J. Chem. Soc.*, **43**, 37 (1883); (c) Delépine and Ville, *Compt. rend.*, **170**, 1390 (1920); (d) Hanson and James, *J. Chem. Soc.*, 1955, 2979 (1928).

(5) Barratt and Stein, *Proc. Roy. Soc. (London)*, **A122**, 582 (1929).

(6) Gillam and Morton, *ibid.*, **A124**, 604 (1929).

than that of the bromine content alone. Assuming the absorption coefficient of the inter-halogen compound to be negligible (exact wave length not stated), Barrett and Stein⁵ calculated equilibrium constants for the dissociation of BrCl, obtaining a mean value of 0.28. We have recalculated their data making an allowance for the absorption of BrCl and find that this value is reduced to a value not greater than 0.18. The results of Gillam and Morton were qualitative but they estimated that the bromine chloride was less than 50% dissociated.

Gray and Style⁷ measured the absorption of gaseous mixtures of Cl₂ and Br₂, finding a similar decrease of the bromine absorption, upon the addition of chlorine. Assuming that at 0.579 μ the absorption of BrCl is negligible, they give for K in two experiments, the value 0.132 and 0.125. Their Table IV follows

Mixt.	Initial (Cl ₂)	Initial (Br ₂)	Free (Cl ₂)	Free (Br ₂)	(BrCl)	K	K'
I	0.0401	0.00539	0.0352	0.00045	0.0098	0.132	0.162
II	.0114	.0115	.0047	.0048	.0134	.125	.126

K is their published figure; K' is one recalculated from their data, using their assumption. If now bromine chloride absorbs slightly at 0.579 μ , e. g., if the ratio $\alpha_{\text{BrCl}}/\alpha_{\text{Br}_2}$ is 0.01, the values of K obtained from their mixtures I and II, respectively, are shown as

Mixt.	Initial (Cl ₂)	Initial (Br ₂)	Free (Cl ₂)	Free (Br ₂)	(BrCl)	K
I	0.0401	0.00539	0.0351	0.000349	0.01008	0.121
II	.0114	.0115	.0456	.00466	.01368	.114

Similar calculations for other assumed ratios of the absorption coefficients give values of K which are shown graphically in Fig. 1. The two experiments give identical results at $K = 0.111$, and the above ratio 0.0124.

Gray and Style also noted the absence of a decrease in pressure upon mixing gaseous bromine and chlorine, which confirms the conclusion that the compound is BrCl, not Br₂Cl₂ or BrCl₃.

W. Jost⁸ has made measurements of the gaseous equilibrium at various temperatures between 0 and 230° using assumptions similar to those of Gray and Style. He gives values for the equilibrium constant at room temperature, ranging from 0.10 to 0.22.

D. M. Yost⁹ has obtained a value of 0.12 to 0.14 for the equilibrium constant at room tem-

(7) Gray and Style, *Proc. Roy. Soc. (London)*, **A126**, 603 (1930).

(8) W. Jost, *Z. physik. Chem.*, **A153**, 143 (1931).

(9) Blair and Yost, *THIS JOURNAL*, **55**, 4489 (1933), and private communications.

perature and estimated the heat of reaction to be about 300 calories.

In the course of an investigation in this Laboratory it was necessary to have an accurate value for the equilibrium constant for the dissociation of BrCl and also values of the absorption coefficient. By the use of wave lengths near 0.50 μ we have found it possible to obtain very consistent results.

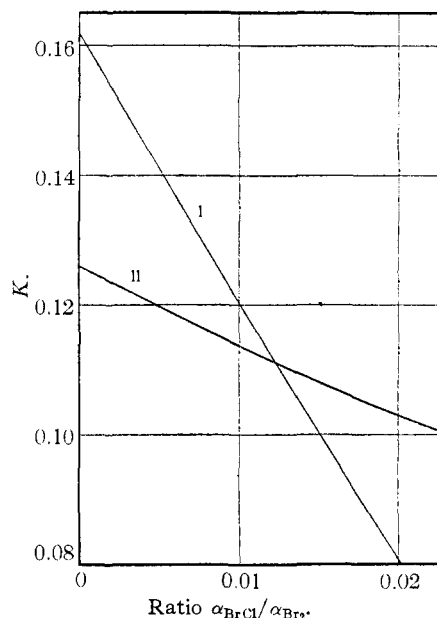


Fig. 1.—Dissociation constant of bromine chloride, recalculated from the data of Gray and Style.

Apparatus and Experimental Procedure

The measurement of absorption was made with a König-Martens spectrophotometer;¹⁰ the shape of reaction vessel was thus fixed. A cylinder of Pyrex glass, 38 mm. inside diameter and 239 mm. long, with fused-on plane parallel ends, was employed. A helium discharge tube¹¹ was arranged to be used end on, with electrodes at right angles from each end. The center portion was 40 cm. long, 0.8 cm. inside diameter. The tube was operated at 80 milliamperes, using a 10,000 volt $\frac{3}{4}$ kw. Thordarson transformer, and gave an intense discharge. The beam passed through a copper chloride-calcium chloride filter solution 1.4 cm. thick (153 g. CaCl₂·4H₂O, 16.7 g. CuCl₂, 1 cc. 2.5 N HCl, 178 cc. H₂O)¹² which removed wave lengths shorter than 0.485 μ , and was focused by two lenses upon the entrance slit of the spectrophotometer.

The lens system and front portion of the spectrophotometer, including the reaction vessel and empty comparison vessel, was placed in a light-tight box, with the helium

(10) Martens and Grunbaum, *Ann. Physik*, **12**, 1004 (1903).

(11) Loaned through the courtesy of Dr. Lloyd T. Jones of the Electrical Products Corporation, Oakland.

(12) Uhler and Wood, "Atlas of Absorption Spectra," Carnegie Inst. Publ. Vol. 71 (1907).

discharge tube on the optical axis, just outside the end of the box; the filter cell was placed on the end wall of the box. Thus no light of shorter wave length than 0.485μ could enter the box, except by opening a shutter placed on the side of the box near the reaction vessel. This side opening was closed as well by a Corning 9-mm. number 586 filter, transmitting only the 0.365μ group of the mercury arc spectrum.

A Cooper-Hewitt 220-volt quartz mercury arc operating on 149 volts, 4.1 amperes, was placed 40 cm. from the reaction vessel, in a nearly horizontal position, so that by opening the shutter the vessel could be illuminated by the 0.365μ lines of the arc. Between the arc and the shutter a Pyrex glass cell, 7.5 cm. thick, 25 cm. long, and 14 cm. high, supplied with running water, was placed. This removed the infra-red radiation from the arc, preventing undue warming of the reaction box.

The spectrophotometer ocular slit was opened wide and the objective double slit was opened sufficiently to cause the images of the slit, formed by the three green lines of the helium discharge, to overlap completely in the field but not wide enough to show the hazy edges of the beam. A uniform field was thus secured. The filter weakened the 0.492μ line considerably; the relative intensities of the three lines, as seen in the spectrophotometer, being 1, 10 and 6 for 0.4922μ , 0.5016μ and 0.5048μ , respectively, giving a center of gravity at 0.5022μ . All three green lines were used because it was found impossible to isolate the strong center line (by narrowing the objective and ocular slits) without reducing the observed intensity below an adequate amount. Since the same light was used throughout the experiments, and since the absorption curve is practically linear over this range of wave length, no appreciable error was thus introduced.

The reaction vessel was connected by a 1.6-mm. capillary side tube with the usual oil and mercury pumps and liquid air trap, a sulfuric acid manometer, and storage vessels for reagents.

The bromine used was Kahlbaum, kept in presence of solid potassium bromide; the chlorine was prepared from anhydrous cupric chloride by heating, and freed from air by freezing out with liquid air and pumping off residual gas; in later experiments the chlorine was also fractionated, with no appreciable effect on the results.

In reading the spectrophotometer, each recorded value of $\log(\tan^2 \theta)$ is the average of at least sixteen settings, eight on each side, of the analyzing nicol prism. The individual settings were usually within 0.2° of the mean. If the settings began to deviate beyond this, resting of the eyes restored accuracy.

In the dark, equilibrium was attained only after periods ranging from sixteen to over sixty hours. The course of one run is given: (Run 18. Initial Cl_2 49.5, Br_2 20.5.)

Time, hours	0	2.3	19.0	23.2	40.5	48	63
$\log I_0/I$ (green)	3.1	2.31	1.476	1.393	1.214	1.180	1.163
		(calcd.)	(obs.)				
$\log I_0/I$ (yellow)	0.291	0.213	0.105	0.102	0.089	0.070	0.071

(The experimental error is greater than the small differences between the last three readings in the

yellow; the green readings are a better indication that equilibrium is not yet reached.)

When illuminated by the 0.365α lines of the mercury arc (about 1000 microwatts falling on the vessel), a steady state was attained after two to five minutes. That this steady state is identical with the thermal equilibrium was proved by: (1) leaving the vessel, after illumination, in the dark for from six to ninety hours more, the absorption remaining constant within the limits of experimental error; (2) illuminating the vessel after attaining thermal equilibrium in the dark, the absorption remaining constant within the limits of experimental error.

It was thus possible to attain the true equilibrium by illuminating under the above conditions for a few minutes, with the advantage that the setting of the spectrophotometer ("blank" reading) does not change appreciably in two or three hours, while it does so to a slight extent overnight or over the several days necessary to be certain of equilibrium attained in the dark. The procedure was then adopted in the actual equilibrium measurements of illuminating until a constant reading was obtained. This was usually accomplished in two minutes, although more time was always allowed.

At one time during the course of the experiments the reaction vessel was removed from the line, and washed with water, alcohol and ether and dried, before replacing it. The next experiments with bromine and chlorine gave the results shown in Table I.

TABLE I

Run	Initial	Values of $\log I_0/I$ (green)		Remarks
		In dark	Then illuminated	
45	1.253	0.485 (15 min.)	0.480 (20 min.)	Complete in dark after about 30 min.
		.479 (60 min.)		
46	1.421	.802 (15 min.)	.383 (0.5 min.) .377 (1.5 min.) .377 (15 min.)	Incomplete in dark after 45 min., complete in light after 1.5 min.
		.541 (45 min.)		
47	1.660	1.492 (15 min.)	.777 (2 min.) .777 (30 min.)	Slowly reacting in dark; complete in light after 2 min.
		1.330 (45 min.)		
48	1.410	1.017 (22 min.)	.374 (0.5 min.) .365 (2 min.) .365 (24 min.)	Reacting more slowly in dark than the identical Run No. 46. Complete in light after about 2 min.
		0.780 (45 min.)		
		.682 (60 min.)		

These observations indicate that immediately after cleaning, the dark reaction proceeded at

least thirty times as fast as before, but that in the course of several experiments the various conditions were gradually restored. It is quite likely, therefore, that the dark reaction is catalyzed by the walls of the vessel. Since the light reaction did not appear to be speeded up appreciably by the cleaning, it is probably homogeneous, although a rigorous proof of this would require further experimentation.

These results are not in agreement with those of W. Jost,¹³ who observed a half time of less than one minute. However, Jost does not mention having taken any precautions to exclude light from his reaction vessel.

Dissociation Constant and Extinction Coefficient of BrCl: Experimental Data and Calculations.—Pressures were recorded in cm. of sulfuric acid (1 cm. = 0.001787 atm.) corrected to a common temperature, 0°, and the thickness of the absorbing layer was 23.9 cm. Applying Beer's law to the mixture we have

$$\log I_0/I = P(\text{Br}_2) + Q(\text{BrCl}) + Z(\text{Cl}_2) \quad (1)$$

for the green lines of the helium discharge, and

$$\log I_0/I = Y(\text{Br}_2) + W(\text{BrCl}) \quad (2)$$

for the yellow lines, where P , Q , Z , Y and W are (0.001787) (23.9) times the corresponding values of the absorption coefficients.

The term $Z(\text{Cl}_2)$ in Eq. (1) was small in our experiments, and was calculated by a first approximation to the chlorine pressure of the mixture. The remainder of the expression was called R : $R = P(\text{Br}_2) + Q(\text{BrCl}) = \log I_0/I - Z(\text{Cl}_2)$.

The values $P = 0.153$, $Z = 0.00009$ and $Y = 0.0142$ were determined directly, using the pure gases.

Preliminary experiments with bromine and chlorine, using the yellow lines at 0.588 μ , and making the same assumption as Gray and Style, and Jost, namely, that the absorption of BrCl is negligible in this region (*i. e.*, that the second term on the right in Eq. 2 is equal to zero), gave the results shown in Table II. Recalculations of the data, assuming various ratios $\alpha_{\text{BrCl}}/\alpha_{\text{Br}_2}$, are also shown, and these results have been plotted, giving curves similar to those in Fig. 1. The curves cross at $K = 0.103$ and 0.105, and ratio $\alpha_{\text{BrCl}}/\alpha_{\text{Br}_2} = 0.017$. These results are similar to those obtained by recalculating the data of Gray and Style, and indicate that the true value of K lies near 0.11.

(13) W. Jost. *Z. physik. Chem.*, **B14**, 413 (1931).

TABLE II

$\alpha_{\text{BrCl}}/\alpha_{\text{Br}_2}$	Initial pressure		Final log I_0/I (yellow)	Final pressure			K
	Br_2	Cl_2		Br_2	BrCl	Cl_2	
0	19.38	67.94	0.042	2.92	32.9	51.5	0.139
0.01				2.58	33.6	51.1	.117
.02				2.24	34.3	50.8	.097
0	19.44	70.6	.041	2.88	33.1	54.0	.142
.01				2.54	33.8	53.7	.119
.02				2.19	34.5	53.4	.098
0	9.80	76.5	.012	0.84	17.9	67.6	.178
.01				.66	18.3	67.4	.133
.02				.47	18.7	67.2	.091

Experiments were then made using the green lines (with a center of gravity at 0.5022 μ). Two types of experiments were performed; in the first type the initial pressure of bromine was low and that of chlorine high, giving a low final bromine pressure, so that as large as possible a portion of the final absorption would be due to BrCl, and the absorption due to Br_2 would be small. This small Br_2 absorption was calculated by assuming a value for the equilibrium constant $K = (\text{Br}_2)(\text{Cl}_2)/\text{BrCl}^2 = x(c - b + x)/(2b - 2x)^2$ where b is initial Br_2 pressure, c is initial Cl_2 pressure and x is final Br_2 pressure; x was thus determined. Then $Q = R - P(\text{Br}_2)/(\text{BrCl})$. Errors in the estimation of the equilibrium constant, if x were small, would introduce only small errors into the value of Q .

In the second type of experiment, the initial pressure of bromine was higher (relative to that of chlorine), so that the final pressure of bromine would be larger, and most of the light absorption by the equilibrium mixture would be due to bromine, that due to bromine chloride being small. The approximation obtained for Q from the average result of type 1 experiments was then inserted in the relation already given, namely, $R = P(\text{Br}_2) + Q(\text{BrCl}) = P(x) + Q(2b - 2x)$, whence $(\text{Br}_2) = x = (R - 2bQ)/(P - 2Q)$, also $(\text{BrCl}) = (2b - 2x)$ and $(\text{Cl}_2) = (c - b + x)$. This gave a second approximation to K , since errors in Q introduced only small errors in the value of K , if the absorption due to BrCl were small.

Using this value of K , a second approximation for Q was obtained from the results of type 1 runs, and so on. The final approximations for Q and K are given in full in Tables III and IV. Results: $K = (\text{Br}_2)(\text{Cl}_2)/(\text{BrCl})^2 = 0.107$. $Q = 0.0164$, whence $\alpha_{\text{BrCl}} = 0.384$, at 0.502 μ .

W. Jost⁸ reported that the presence of air or other foreign gases (hence presumably of Cl_2 and BrCl) increased the extinction coefficient of

TABLE III
 EXPERIMENTAL DATA, RUNS OF TYPE 1. FINAL APPROXIMATIONS FOR Q . (ASSUMED $K = 0.107$)

Initial pressure in cm. of H_2SO_4		Final $\log I_0/I$	Part due to Cl_2	Diff. R	Final (Br_2) = x	Final ($BrCl$) = $2(b-x)$	Part of R		Q
b, Br_2	c, Cl_2						due to Br_2	due to $BrCl$	
10.05	76.0	0.403	0.006	0.397	0.582	18.95	0.089	0.308	0.0163
9.8	76.5	.397	.006	.391	.546	18.5	.084	.307	.0166
9.3	73.9	.371	.006	.365	.506	17.6	.078	.287	.0163
9.2	75.6	.366	.006	.360	.488	17.45	.074	.286	.0164

Av. 0.0164

 TABLE IV
 EXPERIMENTAL DATA, RUNS OF TYPE 2. FINAL APPROXIMATIONS FOR K . (ASSUMED $Q = 0.0164$)

Initial pressure in cm. of H_2SO_4		Final $\log I_0/I$	Part due to Cl_2	Diff. R	$x = \frac{R - 2bQ}{P - 2Q}$	($BrCl$) = $2(b-x)$	(Cl_2) = $c - b + x$	K
b, Br_2	c, Cl_2							
19.5	70.95	0.927	0.005	0.922	2.36	34.25	53.8	0.1080
19.5	69.75	.929	.005	.924	2.36	34.30	52.6	.1057
10.9	9.25	.944944	4.88	12.07	3.21	.1078
11.0	9.25	.958958	4.96	12.07	3.23	.1102
8.25	17.2	.480	.001	.479	1.72	13.06	10.67	.1076
10.85	13.8	.777777	3.50	14.68	6.44	.1048
12.2	18.1	.818	.001	.817	3.46	17.48	9.36	.1060
11.0	14.85	.769769	3.39	15.20	7.25	.1054

Av. 0.107

bromine at wave length 0.575μ by 5 to 12%. To determine whether this occurred under the conditions of our experiments, 7.3 cm. of bromine was admitted to the reaction vessel, the extinction measured, and air then admitted to a total pressure of one atmosphere. Allowing 0.5% increase for bromine swept from the capillary to the vessel by the air, the absorption remained constant within the limits of experimental error (dropped 0.1% at 0.502μ , dropped 0.5% at 0.588μ). It must be concluded that the effect reported by Jost is absent under the conditions of pressure and illumination in these experiments.

As to the absorption of $BrCl$ at 0.588μ , a check of $\log I_0/I$ in nineteen runs in which the equilibrium mixture of bromine, chlorine and bromine chloride was present, and in which the concentration of bromine and bromine chloride was known independently using the absorption in the green and the above constants, showed that in the yellow a definite absorption was present, in addition to that which could be ascribed to bromine. Although the degree of accuracy obtainable was low, values of W ranging from 0.00013 to 0.00055, corresponding to $\alpha = 0.003$ to 0.013, were obtained. This is just the conclusion to be reached from Fig. 1, and from Table II, and explains the higher values of K obtained by Jost and others using readings in the yellow.

Since the heat of reaction was found by Jost to be approximately 300 calories, the box was not controlled in temperature by any special arrangement, but the temperature remained constant at $28 \pm 2^\circ$, thus introducing less than 1% error in K .

Summary

Previous work on the dissociation constant of bromine chloride is discussed, and it is shown that the values of the dissociation constant for gaseous $BrCl$, obtained by measuring the extinction of the equilibrium mixture at 0.58μ , are probably about 30-60% high, owing to the assumption that the extinction of the mixture is due entirely to Br_2 .

Using the green lines of the helium discharge, with center of gravity 0.502μ , as transmitted by the filter used, the dissociation constant and extinction coefficient of gaseous $BrCl$ were measured together, by suitable variation of the pressures used. At this wave length the ratio $\alpha_{BrCl}/\alpha_{Br_2}$ is about 0.1, so that α_{BrCl} may be measured with reasonable accuracy. At 28° the values $K = (Br_2)(Cl_2)/(BrCl)^2 = 0.107 \pm 0.002$, and $\alpha = \log I_0/I$ for 1 cm. layer of gas corrected to 1 atm., $0^\circ = 0.384 \pm 0.006$, were found.

It was observed that equilibrium was attained only after several hours in the dark, but this was reduced to about two minutes by illuminating with the 0.365μ lines of the mercury arc, or to about thirty minutes by freshly cleaning the walls

of the reaction vessel, without illumination. That the steady state in the light is identical with the thermal equilibrium, is shown by the fact that

no shift occurs in the dark after illumination, or in the light after attaining equilibrium in the dark.

BERKELEY, CAL.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Low Pressure Data of State of Nitric Oxide and of Nitrous Oxide between their Boiling Points and Room Temperature

BY HERRICK L. JOHNSTON AND HARRY R. WEJMER

Comparatively little has been published on the P - V - T relationships in real gases below the ice point. Such data as do exist relate, for the most part, to the few gases commonly employed in gas thermometry and to high pressure isothermals of industrially important gases. In conjunction with a program of accurate low temperature heat capacity measurements of gases by the velocity of sound method, now in progress in this Laboratory, it has been found necessary to determine for ourselves the necessary corrections for gas imperfection. The present paper gives a description of the apparatus and procedure used, followed by the results obtained with nitric oxide and with nitrous oxide.

Preparation and Purification of the Gases

Nitric Oxide.—We prepared nitric oxide by the procedure followed by Johnston and Giaque¹ which combines the chemical process of Winkler² with the highly efficient distillation and sublimation process of Gray.³ We employed "reagent quality" or high grade "C. P." chemicals as reagents. The capacity of our preparation and purification system was about one-fourth that of Johnston and Giaque but in other respects it was identical in construction and we employed the same technique in its operation. Hence we think it reasonable that the quality of our nitric oxide was approximately the same as that of those authors (*i. e.*, the mole fraction of impurity less than 0.00001).

Nitrous Oxide.—We prepared nitrous oxide by the method of Gehlen,⁴ which consists in the addition of sulfuric acid to a slightly alkaline aqueous solution of the normal potassium salt of nitrosylsulfuric acid. A consideration of the facts presented in Gehlen's paper, in conjunction with a careful search of the literature, convinced us that this method yields a product of higher purity than is given by the methods more commonly in use. Our preparation line, which was made of Pyrex glass with fused joints and was previously flushed and evacuated, consisted of a five-liter generating flask con-

taining a saturated solution of potassium nitrosylsulfite into which 50% sulfuric acid was added, dropwise, and the following units for the preliminary purification: a trap cooled with dry ice-ether, a bead tower with 50% potassium hydroxide, a bead tower with 90% sulfuric acid, a second dry ice-ether trap, a storage bulb in which the liquid was condensed, by means of liquid air, to a colorless liquid, and a freshly charged phosphorus pentoxide drying column. The final stage of purification was carried out by circulating the product, four times, through the identical distillation and sublimation cycle employed with the nitric oxide.

The potassium nitrosylsulfite was prepared by introducing nitric oxide, produced in the manner described earlier except for the physical purification which was omitted, into a 40% solution of potassium sulfite which was, likewise, 5% in potassium hydroxide. The crystals obtained by this process were washed with a 5% potassium hydroxide solution and were, eventually, redissolved to form the charge for the generating flask.

As with the nitric oxide, only "reagent quality" or "C. P." chemicals were employed; the distilled water used to make up solutions (or the solutions themselves) was boiled to exclude air and we followed the same general technique described by Johnston and Giaque.¹

While we had available no convenient method of estimating small traces of impurity we think it probable that the final product was comparable, in purity, with the nitric oxide.

Hydrogen, used to calibrate the resistance thermometer, was taken from a commercial tank of electrolytic hydrogen and was purified by slow passage through high grade charcoal cooled with liquid air. The charcoal was previously degassed with a stream of hydrogen at a temperature a little below red heat.

Method and Apparatus

Our method is based on the use of the constant volume gas thermometer wherein the same equipment is used for both hydrogen, whose properties as a real gas are known, and the gases of interest whose P - V - T properties we desired to ascertain. The calibration of a sensitive electrical resistance thermometer was secured when hydrogen was used in the apparatus, thereby establishing the true temperature when the nitrous and nitric oxides were under measurement.

Figure 1 is a diagram of the apparatus, which is modeled after the constant volume gas thermometer of Giaque.

(1) Johnston and Giaque, *THIS JOURNAL*, **51**, 3194 (1929).

(2) Winkler, *Ber.*, **34**, 1408 (1901).

(3) Gray, *J. Chem. Soc.*, **87**, 1601 (1905).

(4) Gehlen, *Eer.*, **65**, 1131 (1932).