

THE ABSORPTION OF NITROGEN DIOXIDE

IN CONCENTRATED NITRIC ACID

by

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532 Beacon Street
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Dear Sir:

I take pleasure in submitting herewith a thesis entitled " The Absorption of Nitrogen Dioxide in Concentrated Nitric Acid ", in partial fulfillment of the requirements for the degree of Bachelor of Science.

Respectfully submitted,

Signature redacted

William R. Stern

ACKNOWLEDGMENT.

The author wishes to express his thanks to Professor L. A. Monroe, under whose suggestion and guidance this investigation was carried out.

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I. SUMMARY

Nitrogen dioxide was absorbed from a mixture in air using 96 % nitric acid and 20 % sodium hydroxide solutions, in a small packed tower, at room temperature and pressure. The observed absorption rates were compared to determine whether gas or liquid film resistance is controlling in the absorption of NO_2 in concentrated HNO_3 , and to get some understanding of what actually takes place in this absorption process.

A new method of gas analysis was used, utilizing the color of NO_2 plus the proper light filter to give fairly accurate readings on a Weston pocket exposure meter. This allows continuous analysis of both inlet and outlet gases, corrections for acid mist being necessary when mist is encountered.

When absorbing nitrogen dioxide in strong nitric acid, much nitric acid mist formation was found in the gas. This probably increased the interfacial area many fold, resulting in very little effective overall resistance to transfer. The unknown increase in transfer area prevents any evaluation of individual film resistances.

Very large overall transfer coefficients, $K_Y a$, for the absorption of NO_2 in strong HNO_3 were found, whose values ranged from 21 to 93 Lb. Mol. NO_2 / Hr. Cu.Ft. (Y).

H.T.U. values, the height of a transfer unit, of

the order of from one to four inches were found for the nitric acid runs.

Much smaller overall transfer coefficients for the absorption in caustic were found, all being in the vicinity of 4 Lb. Mol. NO_2 / Hr. Cu.Ft. (Y). H.T.U. values in the neighborhood of 2 feet were found for the caustic absorption.

Confidence is placed in the validity of the experimental results because of the fairly good material balance of most of the data.

II. INTRODUCTION

Many workers have investigated the absorption of nitrogen dioxide in aqueous solutions, but essentially no work has been done upon the absorption of the gas in very strong nitric acid. The previous workers were primarily interested in the absorption of the gas, followed by various reactions with water to form nitric acid of various strengths up to 68 per cent nitric acid.

It is the province of this project, however, to study the absorption of NO_2 in HNO_3 of such strength that the reactions with water are negligible because of the extremely low water concentration. Information concerning this process is needed to permit accurate design of equipment for a recently proposed method for the manufacture of strong nitric acid. ¹

A study of absorption is based upon certain principles. Matter is transferred from the gas to the liquid through the surface dividing the two phases. A clearer picture shows a relatively stationary gas film next to the gas - liquid interface, and a somewhat still liquid film beyond that, while the bulk of the liquid and gas are in a relatively turbulent state of flow. Matter, nitrogen dioxide in this case, passes through the bulk of the gas mainly by convection to the rather stationary gas film. Here the transfer is mainly by molecular diffusion to the gas - liquid interface, and similarly through the liquid film and into the bulk of the liquid. ²

The main resistance to mass transfer lies in the two stationary films, where the rate of transfer is proportional to the concentration gradient in the films. At the interface between the phases, transfer of material depends upon the equilibrium relation between the phases. The equilibrium relation of NO_2 and strong nitric acid is found to be that of Henry's Law, which states that the pressure of nitrogen dioxide over $\text{HNO}_3 - \text{NO}_2$ mixtures is proportional to the NO_2 concentration for small amounts of nitrogen dioxide. ³

An equation for mass transfer through the stationary gas film may be set up,

$$- \frac{dN}{dA} = k_Y (Y - Y_1) \quad (1)$$

From this fundamental equation, the equation used in finding the transfer coefficients in this study, ⁴

$$K_Y a = \left(\frac{G}{Sl} \right) \frac{Y_{\text{ent.}} - Y_{\text{leav.}}}{(Y - Y^*)_{\text{l.m.}}} \quad (2)$$

is developed for the case where the equilibrium curve is essentially a straight line..

III. PROCEDURE

Apparatus.

The absorption was carried out in a small glass tower, 2.3 inches in diameter, packed to a height of one foot with three eighth inch Raschig Rings. Air, used as the diluting gas, was obtained from the compressed air line, and passed through the tower countercurrent to the liquid flow. The nitrogen dioxide was kept in a chrome steel bomb, and was expelled at a constant rate into the entering air stream.

Gas Analysis.

As is shown in Figure I, the mixture of gases passed through the analysis flasks both before entering and after leaving the tower. The light, lens, filter, and exposure meter were mounted on a sliding track, as shown in Figure II, so that the apparatus could be moved back and forth at intervals to analyze the gases alternately. Space was left between the flasks so that a calibration reading could be frequently taken and the light kept adjusted at the proper intensity. Due to mist formation in the acid runs, the outlet gases had to be corrected for the decrease in effective intensity.

Liquid Analysis.

The NO_2 content of the acid was measured by the addition of a known amount of $\text{Ce}(\text{SO}_4)_2$ in 60 % H_2SO_4 , to be followed later by titration to an excess of FeSO_4 .

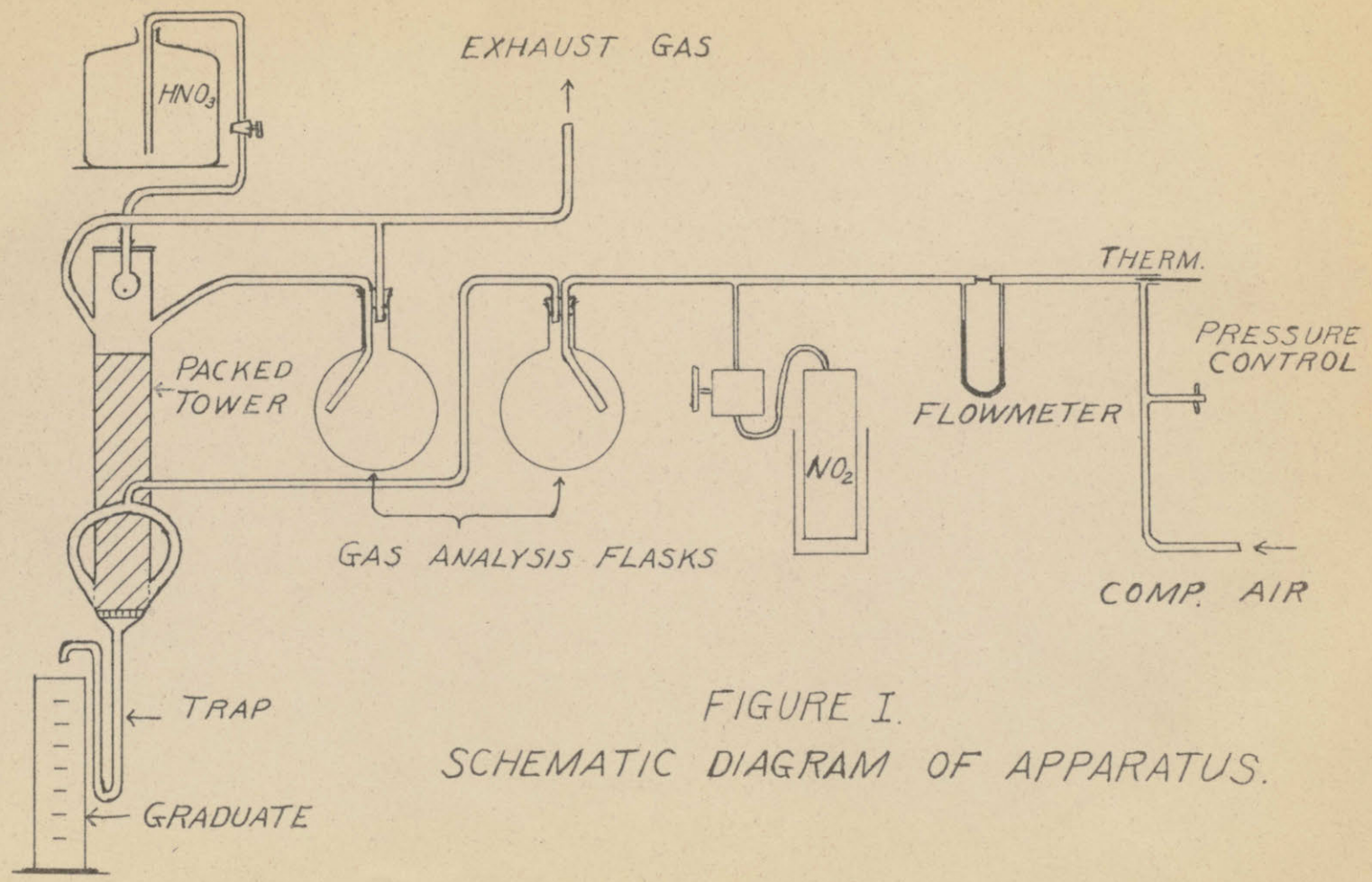


FIGURE I.
SCHEMATIC DIAGRAM OF APPARATUS.

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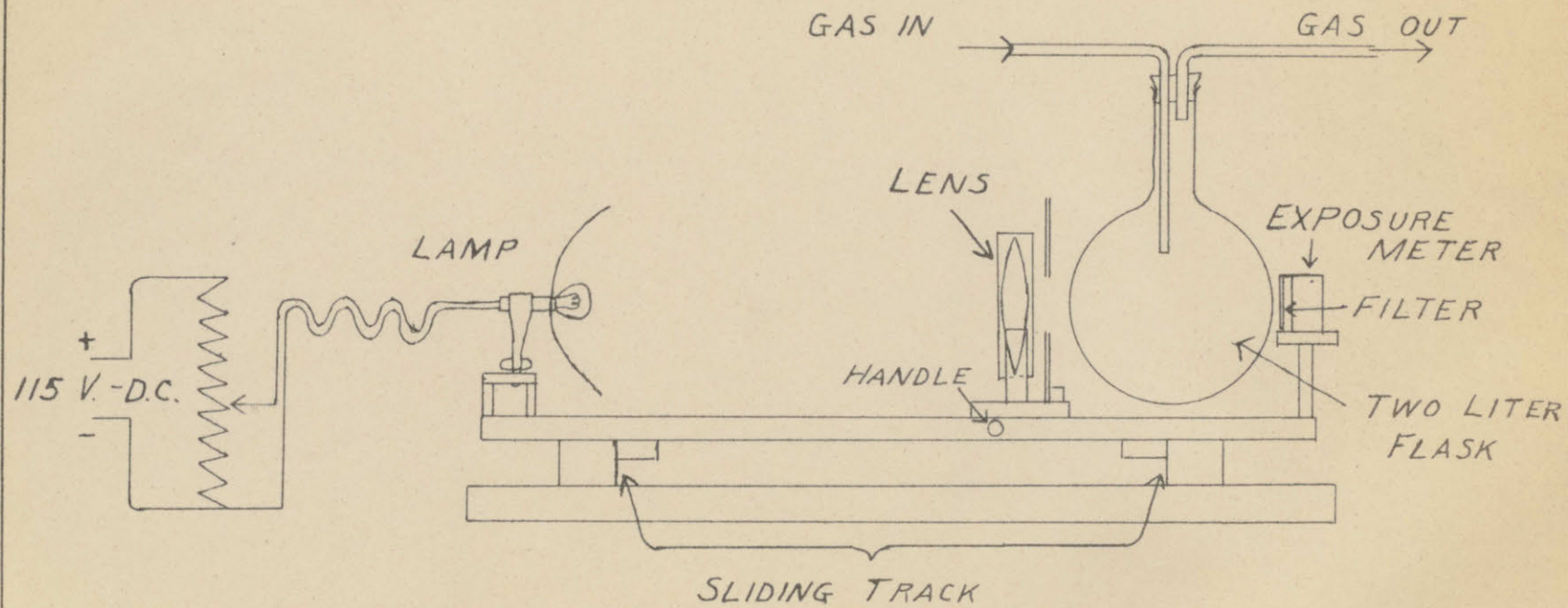


FIGURE II. APPARATUS FOR GAS ANALYSIS.

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The NO_2 content of the caustic was measured by acidifying with H_2SO_4 , adding a known quantity of KMnO_4 , and titrating to an excess of FeSO_4 .

Laboratory Procedure.

Six runs were made using strong HNO_3 and five runs were made using 6 N. NaOH . Gas and liquid rates were kept constant throughout any single run. Samples of liquid were taken before the NO_2 was admitted to the air line, these liquid samples being used as representative of the liquid entering the tower. Nitrogen dioxide was then admitted to the air stream, constant conditions attained, and then the exiting liquid was run into a graduate for a certain time. The graduate was then removed and the liquid analyzed for its NO_2 content.

Temperatures of air entering and leaving, and of liquid entering and leaving was noted. Inlet and outlet gases were continually analyzed throughout each run. It was not difficult to keep the entering gas analysis constant, by means of the light meter and the throttling valve on the NO_2 container. It was necessary to keep the nitrogen dioxide bomb at about 37°C . to expell the NO_2 . This was accomplished by means of a constant temperature water bath.

Evaluation of Data.

As developed in the introduction of this report, the values obtained experimentally for the transfer

coefficients according to the equation for mass transfer,

$$- dN = k_Y a S dl (Y - Y_1) = K_Y a S dl (Y - Y^*) \quad (1 b)$$

were evaluated from the integrated form, ⁴

$$K_Y a = \left(\frac{G}{S l} \right) \frac{Y_{ent.} - Y_{leav.}}{(Y - Y^*)_{l.m.}} \quad (2)$$

as derived when Henry's Law applies, from

$$G dY = K_Y a S dl (Y - Y^*) \quad (3)$$

Transposing,

$$\int \frac{dY}{Y - Y^*} = \frac{K_Y a S}{G} \int dl \quad , \quad (4)$$

the integral, $\int \frac{dY}{Y - Y^*}$, may be approximated as equal to

$$\frac{Y_{ent.} - Y_{leav.}}{(Y - Y^*)_{l.m.}} \quad , \quad \text{and}$$

$$\frac{Y_{ent.} - Y_{leav.}}{(Y - Y^*)_{l.m.}} = \frac{K_Y a S l}{G} \quad . \quad (2 b)$$

Since $\int \frac{dY}{Y - Y^*}$ is equal to the Number of Transfer Units, commonly called the N.T.U., corresponding evaluations of the integral shown above may be used to represent the N.T.U. .

The above method of calculating $K_Y a$ may be applied to the absorption of NO_2 in caustic solutions also. Recent work has shown gas film resistance to be controlling in this case, ⁵ and indeed the caustic solution leaving the tower hardly even smelled of NO_2 . Since Y^* is then equal

to zero, the

$$\int \frac{dY}{Y - Y^*} = \int \frac{dY}{Y - 0} = \int \frac{dY}{Y} = \ln \frac{Y_{ent.}}{Y_{leav.}} \quad (5)$$

and

$$K_Y a = \left(\frac{G}{Sl} \right) \ln \frac{Y_{ent.}}{Y_{leav.}} \quad (6)$$

for the absorption of NO_2 in 20 % sodium hydroxide solutions.

Preparation of Materials.

All of the nitrogen dioxide used was prepared in the laboratory by the reaction of fuming nitric acid upon arsenious trioxide in the presence of concentrated sulphuric acid. The gas was passed through phosphoric oxide, condensed, and redistilled through phosphoric oxide.

The strong nitric acid was procured through the courtesy of the Monsanto Chemical Company.

IV. RESULTS

Six runs were made, absorbing NO_2 from mixtures in air by 96 % HNO_3 . The results of these runs are listed in Table I.

Five runs were made, using 20 % sodium hydroxide solutions to absorb NO_2 from mixtures in air. The results of these runs are tabulated in Table II.

The original data of all the runs are evaluated in Table III.

TABLE I.
RESULTS OF ACID RUNS.

RUN NO.	LIQUID COMPN:		LIQUID TEMP.		Y [*]	
	$\frac{\text{Lb. Mol. NO}_2}{\text{Cu. Ft.}}$		° Cent.		$\frac{\text{Mol. NO}_2}{\text{Mol. Air}}$	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
1	.00343	.04877	20	13.5	.0023	.0227
2	.00362	.0485	20	13	.0024	.0227
3	.00293	.0346	20	14	.0020	.0170
4	.0101	.0293	20	14	.0066	.0146
5	.00413	.0311	20	14	.0026	.0158
6	.00400	.0331	20	14	.0025	.0167

RUN NO.	LIQUID FLOW	GAS FLOW	Y	
	$\frac{\text{Lb. Mol. Acid}}{\text{Hr. Sq. Ft.}}$	$\frac{\text{Lb. Mol. Air}}{\text{Hr. Sq. Ft.}}$	Inlet	Outlet (calc.)
1	7.2	10.2	.0272	.0036
2	7.0	10.2	.0272	.0044
3	7.2	5.1	.0272	---
4	7.0	5.1	.0272	.0077
5	10.8	10.2	.0272	.0061
6	11.0	10.2	.0272	.0040

RUN NO.	N.T.U.	H.T.U.	K _{ya}
	$\frac{Y_{\text{ent.}} - Y_{\text{leav.}}}{(Y - Y)_{1.m.}}$	$\frac{12}{\text{N.T.U.}}$ in inches	$\frac{\text{Lb. Mol. NO}_2}{\text{Hr. Cu. Ft. (Y)}}$
1.	9.14	1.3	93
2	8.20	1.5	83.5
3	---	---	---
4	4.14	2.9	21
5	3.16	3.8	32
6	5.00	2.4	51

TABLE II.
RESULTS OF CAUSTIC RUNS.

RUN NO.	LIQUID COMPN: [★]		LIQUID FLOW	GAS FLOW
	Inlet	Outlet		
7	.0007	.0169	9.4	10.2
8	.0023	.0100	9.6	5.1
9	.0009	.0170	9.4	5.1
10	.0031	.0104	17.9	10.2
11	.0013	.0105	20.7	10.2

RUN NO.	Y Inlet	Outlet	N.T.U.	H.T.U.	K _Y a
				in Feet	
7	.0272	.0192	.35	2.85	3.6
8	.0272	.0130	--	--	--
9	.0272	.0112	.89	1.1	4.5
10	.0272	.0205	.28	3.6	2.9
11	.0272	.0173	.45	2.2	4.6

★ All Units are same as in Table I, except H.T.U..

TABLE III.

MATERIAL BALANCE OF ORIGINAL DATA.

RUN NO.	NO ₂ LOST FROM GAS	NO ₂ GAIN. BY LIQ.	RATIO <u>Large exch.</u> <u>Small exch.</u>
	<u>Lb. Mol. NO₂</u> <u>HR.</u>	<u>Lb. Mol. NO₂</u> <u>Hr.</u>	
1	.0066	.0070	1.06
2	.0060	.0068	1.13
3	.0025	.0048	1.92
4	.0025	.0029	1.16
5	.0073	.0062	1.18
6	.0063	.0069	1.09
7	.00241	.00238	1.01
8	.00201	.00118	1.70
9	.00185	.00239	1.29
10	.00268	.00201	1.33
11	.00324	.00292	1.11

V. DISCUSSION OF RESULTS.

It is seen from the tabulation of material balances, Table III, that all of the runs except Nos. 3 and 8 check fairly well, and that runs Nos. 1, 6, and 7 check very well as to the amount of NO_2 lost from the gas equalling the amount gained by the liquid. However, more confidence is placed in the liquid than in the exit gas analysis, and the outlet gas compositions have all been calculated by material balances for the purpose of calculating K_{Ya} and H.T.U. values. The results given in Tables I and II are calculated on this basis, but it should be borne in mind that the corrections do not deviate to any great extent from the observed data.

Validity of the calculated results depends also upon the equilibrium data for nitrogen dioxide - nitric acid,³ and the assumption that there is no appreciable equilibrium vapor pressure of NO_2 above the caustic at any time.

The values obtained experimentally for the transfer coefficients need not be corrected for wall effects, since a comparison of data found by Holloway with that found by Allen⁶ indicates a very small wall effect in a tower similar to the one used in this investigation. As indicated by Holloway,⁶ as long as the packing size is kept small in respect to the diameter of the tower, the values obtained experimentally for the absorption coefficients will hold reasonably well for large towers.

Inspection of the experimentally determined values of the transfer coefficients would indicate large resistance to transfer in the caustic runs and little resistance in the acid runs. Although it is undoubtedly true that the acid runs offered little resistance to NO_2 transfer, recent work has shown the gas film resistance to be controlling in the caustic runs,⁵ indicating little liquid film resistance when using 20 % sodium hydroxide solutions. A large transfer coefficient would then be expected for the caustic runs, since resistance would be encountered to any extent only in the gas film. Using the caustic coefficient as $k_g a$ for the gas film, and the acid overall coefficient, $K_g a$, and applying Henry's Law to the solution of NO_2 in very strong HNO_3 ,³ one can theoretically find the acid film resistance, $\frac{1}{Hk_L a}$, from the resistance equation,

$$\frac{1}{K_g a} = \frac{1}{k_g a} + \frac{1}{Hk_L a} \quad (7).$$

The use of the experimentally determined coefficients, converted from $K_Y a$ to $K_g a$ units, in this equation would be inconsistent, however, since the liquid film resistance would result in a negative, meaningless figure. This discrepancy may be explained as the effect of any or all of three possible errors in the derivation of the coefficients. One, the gas phase resistance may not have been controlling when absorbing NO_2 in the 20 % caustic.

A large liquid film resistance would then increase the transfer resistance which was used in the above equation as the gas film resistance for the acid runs. This has already been discussed. Two, the NO_2 - HNO_3 equilibrium data may have been so inaccurate as to produce fantastic results. This is highly doubtful in view of the acid run results of Table I, where the acid analyses show at all times an equilibrium pressure of NO_2 over the entering or exiting acid that is less than the pressure of the nitrogen dioxide of the gases in contact with the acid. Three, there was considerable nitric acid mist formation in the gas phase during the nitric acid runs. This visible mist was of such an amount as to require a correction in the outlet gas analysis for the decrease in effective intensity of the light reaching the exposure meter.

The most probable hypothesis for the explanation of the discrepancy of the results centers about the mist formation in the gas phase. Mist in the tower might well act as a carrier between the gas and the liquid films. The interfacial area would be increased many fold, due to the nature of such a disperse state, and mass transfer would be correspondingly increased. The liquid and gas streams, flowing countercurrent to each other, undergo close contact and a fair degree of turbulence as they pass through the tower. A small nitric acid droplet formed at the base of the tower, where the air enters, would then pass up with the gas for a short time, absorb

a relatively large amount of NO_2 , and soon approach an NO_2 equilibrium pressure with the surrounding air. After passing a short distance through the tower, the mist particle, relatively large, would enter the liquid film, as a result of its inertia causing the particle to follow a straight line motion through the gas stream. This action would take place all along the tower, resulting in a large transfer of nitrogen dioxide from the gas to the nitric acid.

To increase the complexity of the situation, an exothermic reaction takes place in the gas phase, as evidenced by the small increase in air temperature as the gas passes through the tower. This effect may be explained as the absorption of NO_2 and HNO_3 in the water vapor present in the entering air. Sherwood and Chambers found a similar effect when absorbing nitrogen dioxide in aqueous solutions. ⁵

Such mist formation would in effect increase the factor, a , which relates the volume of the tower to the interfacial surface. Since the evaluation of the resistance equation (7) depends upon the constancy of this factor, the impossibility of such an evaluation is apparent.

Any conclusion as to whether gas or liquid film resistance is controlling in the absorption of nitrogen dioxide in strong nitric acid cannot be drawn from the experimental results. It can be seen, however, that nitric

acid fumes and droplets in the bulk of the gas form a much larger transfer surface. Furthermore, the effective distance between the transfer surfaces is decreased, and increased transfer through the bulk of the gas should be expected. The gas phase resistance encountered in the acid runs would therefore be nowhere the size of the gas phase resistance of the caustic runs. This effect is well brought out by the experimental results. In all the acid runs, the outlet gases contained little more nitrogen dioxide than that corresponding to the equilibrium pressure of NO_2 over the entering acid, which was in contact with the exiting gases. In the caustic runs, however, the exiting gas concentration was far above any such equilibrium. Table III shows that for corresponding liquid and gas rates, two to three times as much NO_2 was transferred in the acid runs than was absorbed in the caustic runs.

Since the gas phase resistance would be much smaller for acid absorption than when absorbing in caustic, overall transfer coefficients should be much larger for the acid absorption. A comparison of Tables I and II shows this to be true. $K_Y a$ s for the absorption in acid ranged from 5 to 20 times the overall transfer coefficients for the caustic runs. Such a large increase in $K_Y a$ is explainable by the fact that the driving forces, $Y - Y^*$, for the acid runs were about one fifth to one tenth those of the caustic runs, and that the difference in entering and leaving gas concentrations, $Y_{\text{ent.}} - Y_{\text{leav.}}$, was about two

to three times as large for the acid runs as for the caustic. Since K_{Ya} was determined by the equation,

$$K_{Ya} = \left(\frac{G}{SI} \right) \frac{Y_{ent.} - Y_{leav.}}{(Y - Y^*)_{l.m.}} \quad (2),$$

substitution of the above values of $Y_{ent.} - Y_{leav.}$ and $Y - Y^*$ in the equation gives K_{Ya} s for the acid runs about five to twenty times those of the caustic runs.

The experimental results also showed that in the caustic runs the Number of Transfer Units contained in the tower averaged about one half, as was expected, with corresponding H.T.U. values, the Height of a Transfer Unit, of about two feet. In the nitric acid runs, however, the N.T.U.s for the same tower ranged from sixteen to five, indicating H.T.U. values of from one to four inches. These results are best explained by the mist formation hypothesis.

Because of the complexity involved and of the relatively small amount of data that was obtained, no attempt was made to correlate K_{Ya} s .

VI. CONCLUSIONS

1. Very large overall transfer coefficients, $K_Y a$, for NO_2 absorption in strong nitric acid were found. The values varied from 25 to 93 Lb. Mol. NO_2 /Hr. Cu.Ft. (Y).
2. Nitric acid mist formation in the gas phase probably increases the interfacial area many fold, resulting in the facts that:
 - a. The overall resistance to NO_2 transfer is found to be very small.
 - b. H.T.U. s for the absorption are only about one to four inches.
 - c. The individual film resistances cannot be determined because of the unknown increase in effective transfer area.
 - d. Overall transfer coefficients for acid and caustic runs, as experimentally determined, cannot be sensibly correlated. The factor, a , in the respective $K_Y a$ s do not represent the the same value.
3. Reasonable overall transfer coefficients for NO_2 absorption in 20 % sodium hydroxide solutions were found. They were all in the vicinity of 4 Lb.Mol. NO_2 / Hr.- Cu. Ft. (Y).
4. H.T.U.s for the caustic absorption were found to be in the vicinity of 2 feet.
5. The validity of the data is evidenced by the material

balances. In most of the runs the NO_2 transfer from the air was within 20 % of that absorbed by the liquid.

6. The continuous flow analysis of NO_2 - air mixtures by a simple photometric device is satisfactory and desirable.

VII. RECOMMENDATIONS

1. All data obtained was for a small tower. This should be kept in mind when applying the transfer coefficients obtained experimentally to the design of larger towers.
2. Further investigation is necessary to ascertain the actual gas and liquid film transfer coefficients for the absorption of nitrogen dioxide in very strong nitric acid.
3. Very large overall transfer coefficients may be expected when absorbing nitrogen dioxide in concentrated nitric acid. The fuming properties of strong nitric acid probably account for the large values obtained.
4. H.T.U. values of the size of a few inches may be expected for the absorption of NO_2 in strong HNO_3 .
5. The continuous flow analysis of NO_2 - air mixtures by a pocket exposure meter is satisfactory and desirable for this type of work.

VIII. APPENDIX

APPENDIX A.

EQUILIBRIUM DATA FOR NO_2 - HNO_3 MIXTURES.

Von Klemence and Rupp³⁸ found the equilibrium data of Table IV for NO_2 - HNO_3 mixtures. The data presented gives total rather than partial pressures over the solutions. The partial pressure of NO_2 has been estimated from the data by assuming Raoult's Law to apply to the HNO_3 throughout the range used, and subtracting the calculated pressure of HNO_3 from the reported total pressure.

The resulting pressures of NO_2 for various strength acids and at various temperatures, listed in Table V, were plotted in Figure III. The $\ln P_{\text{NO}_2}$ was plotted versus the temperature, since it was noted that the straight lines of Figure III would result.

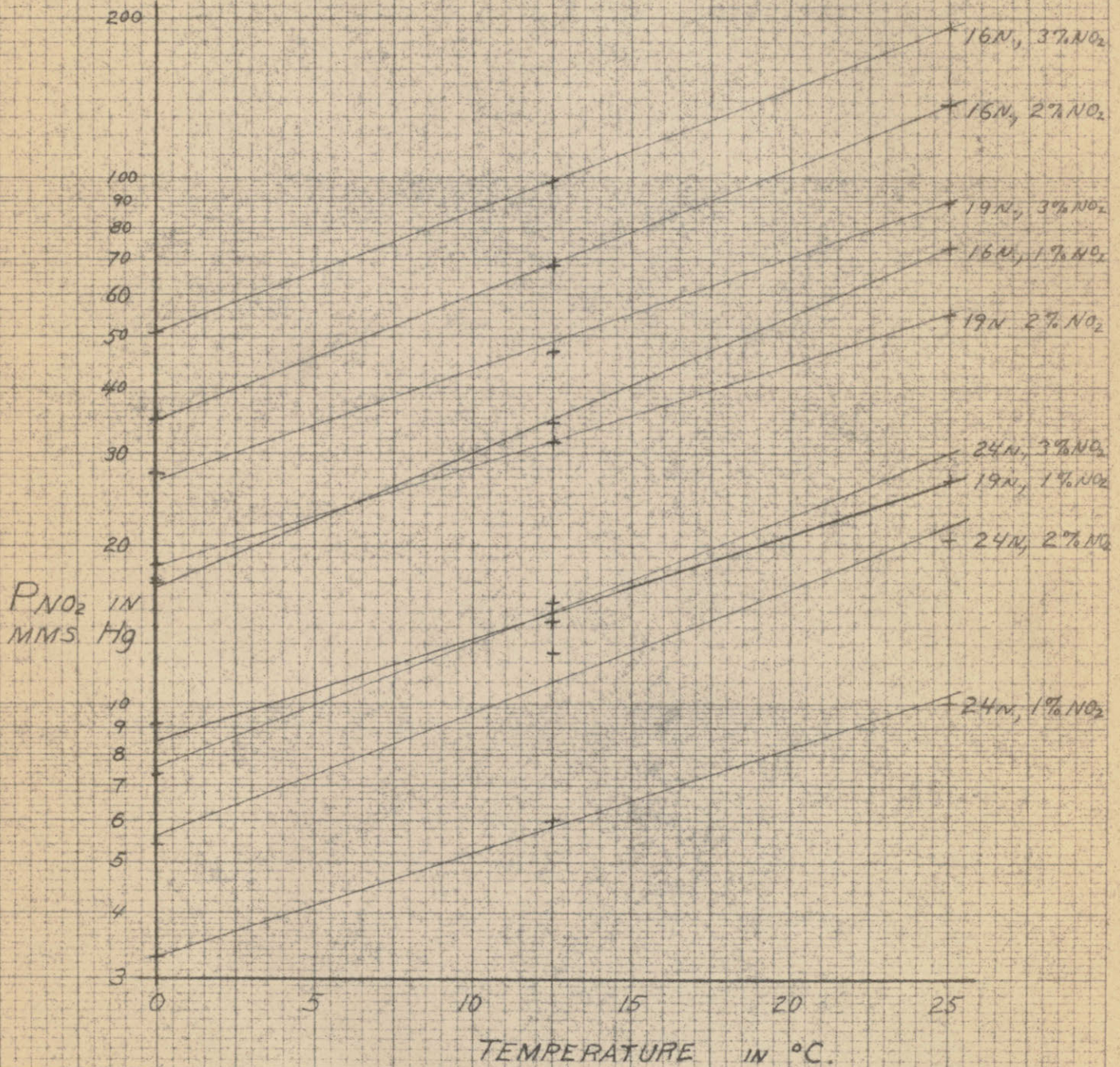
However, Figure III, since it plots logarithms of the pressure, cannot be used to find the pressure of NO_2 over dilute solutions of NO_2 in acid. Since the acid used in the thesis was 23 normal, (96 % acid), and entered the tower at 20 ° Cent., points from Figure III for 23 N. acid were plotted in Figure IV as the pressure of NO_2 versus NO_2 concentration. The resulting curve, the straight line of Henry's Law, passes through the origin, and the pressure of NO_2 over small concentrations of NO_2 may be determined.

TABLE IV.

PRESSURE OF NO_2 OVER HNO_3 .Data of Klemence and Rupp.⁸

WT. % NO_2 ..	Total Pressure in mm. Hg.		
	0 ° C.	12.5 °	25 °
24 N. (100 %) HNO_3			
0	15.9	31.5	62.1
1	19.0	37.2	71.5
2	21.0	42.5	81.5
3	22.8	46.1	88.4
4	24.0	48.9	93.5
5	25.2	51.0	97.9
19 N. HNO_3			
0	6.9	12.7	23.4
1	16.	27.	50.
2	25.	44.	78.
3	35.	59.	106.
4	44.	74.	135.
5	53.	90.	164.
16 N. HNO_3			
0	--	2.2	--
1	17.	36.	80.
2	35.	68.	138.
3	51.	100.	190.
4	67.	129.	236.
5	83.	157.	278.

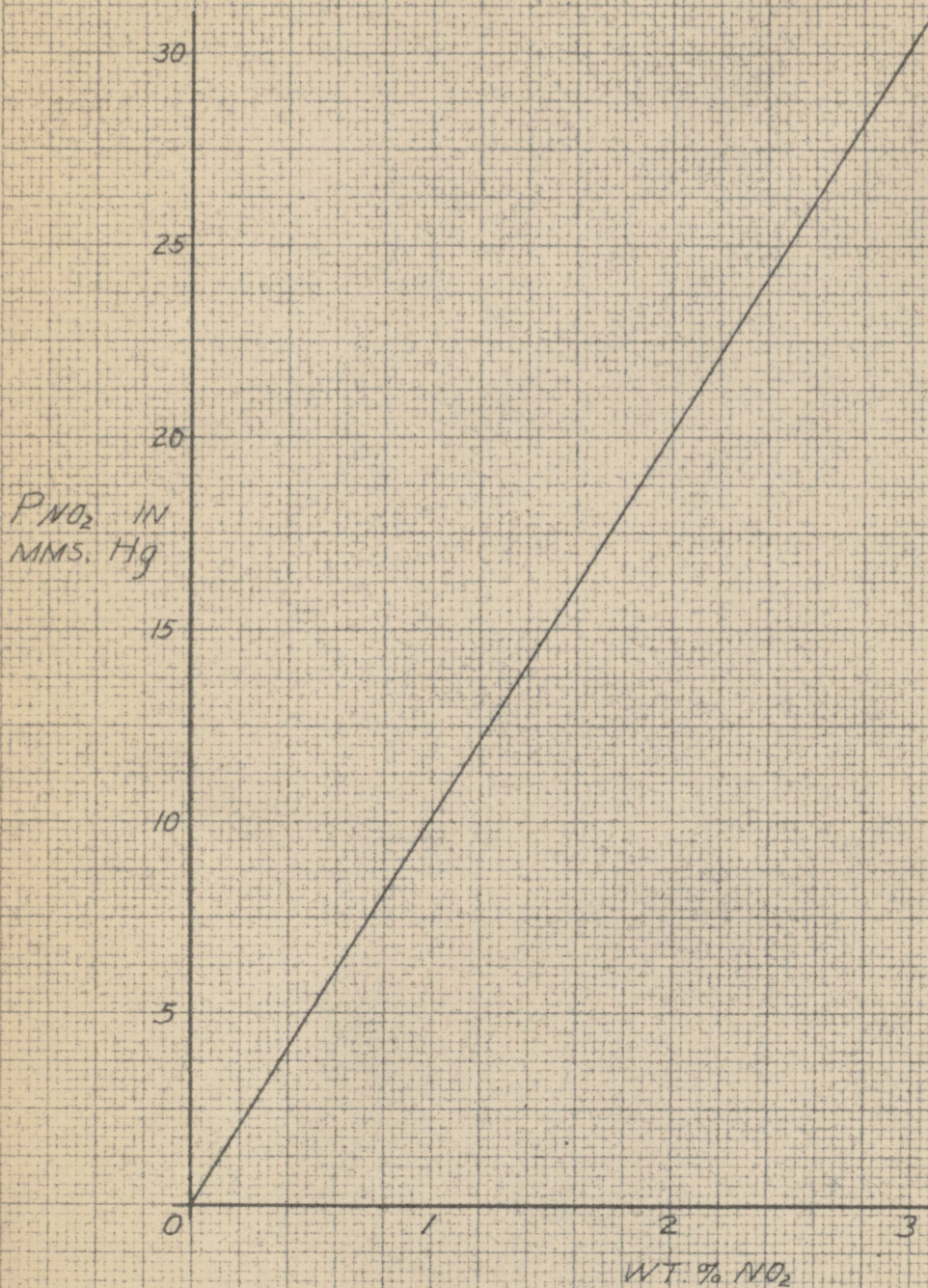
FIGURE III.
PRESSURE OF NITROGEN DIOXIDE OVER NITRIC ACID
FROM DATA OF KLEMENC AND RUPP.³



W.R. STERN
MIT MAY 3, 1940

FIGURE IV

PRESSURE OF NO_2 OVER 23N. HNO_3 AT 20°C .
FROM FIGURE III.



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APPENDIX B.

CALIBRATION OF INSTRUMENTS.

1. GAS ANALYSIS APPARATUS.

NO_2 , kept in a stainless steel bomb, was fed into a compressed air line leading to the gas analysis flask. A thermometer was suspended in the flask, out of the light beam, and the gas analysis flask was connected to a liter flask of measured volume. The gases were then piped to the hood.

The meter reading was taken through the empty flask and without the flask in the beam often, to verify constant light source and the readings recorded. Then a mixture of NO_2 and air was passed through the flasks until the exposure meter reading was constant. The meter reading and temperature were recorded and the flow then quickly shut off. The contents of the flask were then analyzed for NO_2 . The calibration data is listed in Table VI. Sample calculations for the gas analysis will be found under sample calculations.

2. FLOWMETER.

A simple constricted orifice mercury manometer was constructed and used to measure the rate of gas flow. It was calibrated against a previously calibrated dry gas meter. The calibration data is listed in Table VII. Since for an orifice meter,

$$V = k \sqrt{2gh} \quad (8),$$

squaring and transposing,

$$h = k' V^2 \quad (8b),$$

and values of h, the height of the mercury column, were plotted against the square of the volumetric rate of flow. The resulting curve was a straight line, from which the calibration curve, Figure VI, was plotted.

TABLE VI.

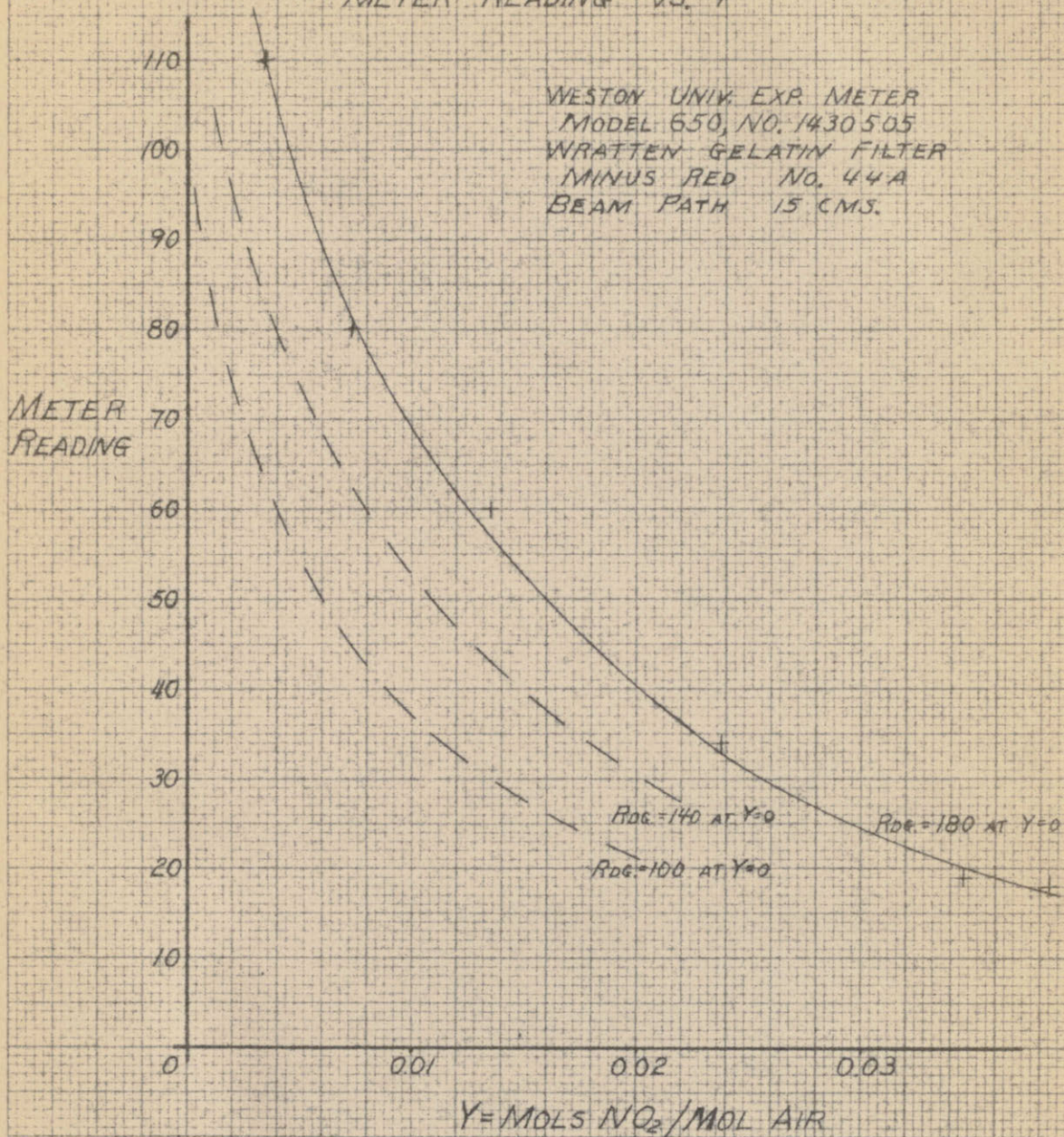
CALIBRATION DATA FOR GAS ANALYSIS APPARATUS.

METER READING			TEMP.	Y
Open Path	Empty Flask	Gas in Flask	° Cent.	$\frac{\text{Mol. NO}_2}{\text{Mol. Air}}$
250	180	19	23	.0324
250	180	110	22	.00329
250	180	18	22	.0357
250	180	115	22	.00282
250	180	34	22	.0223
250	180	60	22	.0126
250	180	80	21	.00683

NOTE.

When mist was encountered, empty flask readings of 140 and 100 were encountered. Curves for these readings were constructed on plot by assuming proportional amount of light transmitted for corresponding meter readings.

FIGURE V.
CALIBRATION CURVE FOR GAS ANALYSIS
METER READING VS. Y



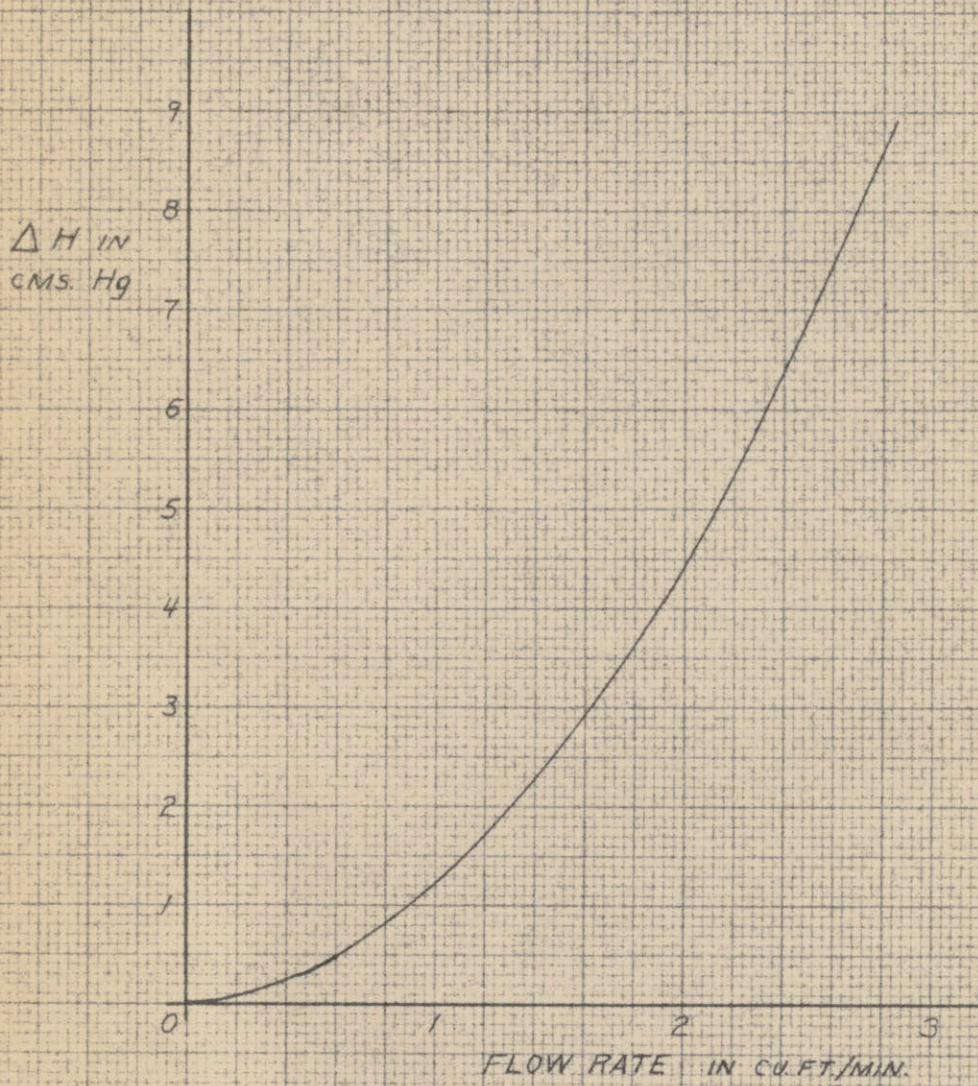
W. R. STERN
M.I.T. APR. 29, 1940

TABLE VII.

CALIBRATION DATA FOR FLOWMETER.

GAS RATE	MANOMETER RDG.
<u>Cu.Ft./Min.</u>	<u>Cm. Hg.</u>
1.10	1.4
1.15	1.5
1.55	2.6
1.85	3.6
2.25	5.6
2.8	8.4

FIGURE VII.
CALIBRATION CURVE FOR FLOWMETER
MANOMETER READING VS. GAS RATE



W.R. STERN
M.I.T. MAY 2, 1940

APPENDIX C.

DISCUSSION OF GAS ANALYSIS APPARATUS.

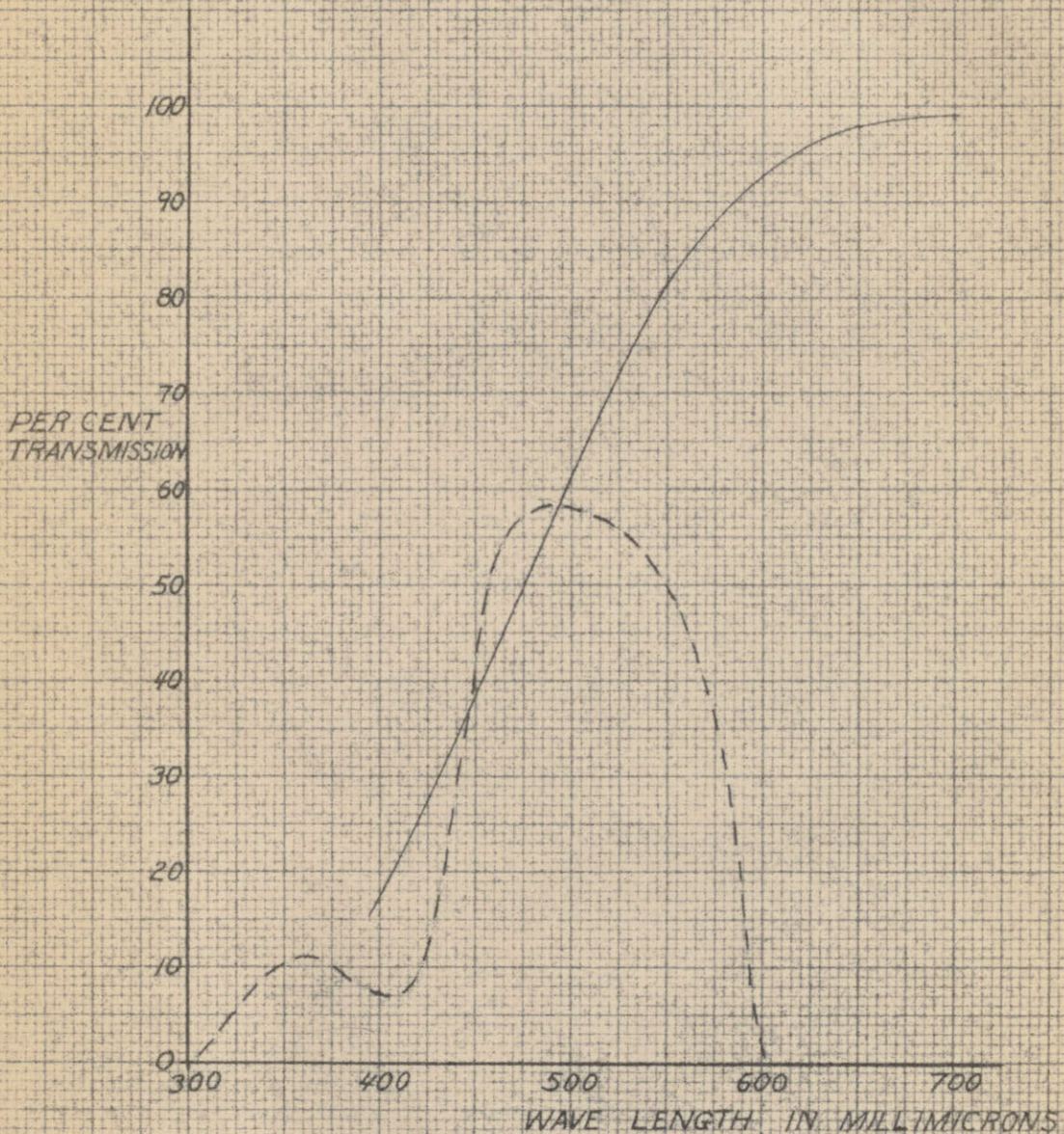
The gas analysis apparatus consists of lamp, filter, and exposure meter, as shown in Figure II. Satisfactory meter readings were found using a 50 c.p. auto lamp, run at over twenty volts, a rather ineffective reflector, and a poor condensing lens. The path of the light beam through the NO_2 - air mixture need only be about 15 cms. to give good results.

Nitrogen dioxide transmits red light, as shown by the solid curve of Figure VII, but a good portion of the greens, wave lengths from 500 to 575 millimicrons, and most of the blues, below 500 millimicrons, are absorbed. Since the light from the lamp has a predominance of the longer wave lengths, light direct from the lamp would pass through NO_2 with little decrease in intensity. If the reds are cut out, however, by a suitable filter, only the blues and greens could be transmitted. Varying concentrations of NO_2 in the light beam would then absorb proportional amounts of the blue - green light, and a sensitive meter reading would result.

The Wratten gelatin filter, Minus Red, No. 44 A, appears to be the most desirable filter attainable. Its transmission curve is represented by the dotted line of Figure VII. The reds are cut out, the blues and greens transmitted, and the filter was found satisfactory.

FIGURE VII.
LIGHT TRANSMISSION CURVES

PER CENT TRANSMISSION VS. WAVE LENGTH
——— FOR NO_2 IN CCl_4 — COURT. COLOR MEAS. LAB., M.I.T.
- - - FOR WRATTEN LIGHT FILTER, NO. 44A
- FROM WRAT. CAT., 15TH ED., E.K.CO.

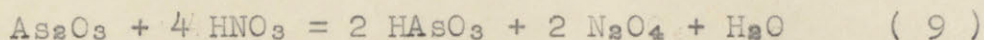


W.R. STERN
MIT MAY 6, 1940

APPENDIX D.

PREPARATION OF NITROGEN DIOXIDE.

Nitrogen dioxide was prepared from the reaction of fuming nitric acid upon arsenious trioxide, according to the reaction,



where the equilibrium reaction,



yields a mixture of NO_2 and N_2O_4 .

The procedure recommended by Prideaux and Lambourne ⁷ was followed. To 250 grams of coarsely powdered arsenious trioxide in a liter flask was added a cooled mixture of 315 grams of fuming nitric acid and 150 grams sulphuric acid. The reaction began slightly above room temperature and required external cooling. A reflux condenser was fitted to effect preliminary cooling of the gas, which was then passed through a U tube containing phosphoric oxide, and then condensed to a liquid in a U tube surrounded by ice and salt. The distillation was stopped before the liquid in the flask turned a green color.

The liquid NO_2 was redistilled, again through P_2O_5 , and the product assumed to be fairly pure NO_2 .

Since the HNO_3 fumes quickly attack cork and rubber, all corks were coated with pycine. The use of pycine is not recommended if any better cement can be produced. I suggest the use of alundum - water glass cement.

APPENDIX E.
ORIGINAL DATA.

The data for all of the runs has been organized
into Table IX.

TABLE VIII.

SUMMARY OF DATA FOR ALL ABSORPTION RUNS.

RUN NO.	LIQUID	L		G	
		<u>Lb. liq.</u> <u>Hr. Sq.Ft.</u>	<u>Lb. air</u> <u>Hr. Sq.ft.</u>	<u>Lb.Mol.Liqd.</u> <u>Hr.Sq.Ft.</u>	<u>Lb.Mol.air</u> <u>Hr.Sq.Ft.</u>
1	96%acid	500	300	7.2	10.2
2	"	500	300	7.0	10.2
3	"	500	150	7.2	5.1
4	"	500	150	7.0	5.1
5	"	750	300	10.8	10.2
6	"	765	300	11.0	10.2
7	6N.NaOH	180	300	9.6	10.2
8	"	180	150	9.6	5.1
9	"	180	150	9.6	5.1
10	"	360	300	19.3	10.2
11	"	360	300	19.3	10.2

RUN NO.	L/G Mol/Mol.	IN TOWER		$Y_{ent.}$	$Y_{leav.}$
		<u>L</u> cc./min.	<u>G</u> cu.ft./min.		
1	0.71	72.	1.90	.0272	.0050
2	0.69	70.	1.9	.0272	.0070
3	1.41	72.	0.95	.0272	.011
4	1.38	70	0.95	.0272	.011
5	1.06	108.	1.90	.0272	.0030
6	1.08	110.	1.90	.0272	.0060
7	0.93	70.	1.90	.0272	.0186
8	1.87	72.	0.95	.0272	.0130
9	1.87	70.	0.95	.0272	.0148
10	1.87	130.	1.90	.0272	.0178
11	1.87	150.	1.90	.0272	.0158

VIII
 TABLE ~~II~~. SUMMARY OF DATA (CONT.) .

RUN NO.	LIQ. ANALYSIS		NO ₂ TRANSFER		LIQ. TEMP.	
	Gm. m.e./10 cc. Inlet	Outlet	FROM GAS Lb. Mol	TO LIQUID NO ₂ /Hr.	° C. Inlet Outlet	
1	.55	7.95	.0066	.0070	20	13
2	.58	7.92	.0060	.0068	20	13
3	.47	5.65	.0025	.0048	20	14
4	1.63	4.76	.0025	.0029	20	14
5	.66	5.06	.0073	.0062	20	14
6	.64	5.38	.0063	.0069	20	14
7	.14	2.71	.00241	.00238	20	-
8	.36	1.60	.00201	.00118	20	-
9	.14	2.72	.00185	.00239	20	-
10	.50	1.67	.00268	.00201	20	-
11	.20	1.68	.00324	.00292	20	-

RUN NO.	Y [*] Mols. NO ₂ /Mol. air		N.T.U.	H.T.U. 1-6 in. 7-11 ft.	K _Y a Lb. Mol. NO ₂ Hr. Cu. Ft.
	INLET	OUTLET			
1	.00235	.0227	8.8	1.2	93
2	.0024	.0227	5	2.4	51
3	.0020	.0170	1.8	6.7	18
4	.0066	.0146	1.5	8.	15
5	.0026	.0153	3.0	4.	31
6	.0025	.0167	3.6	3.3	37
7	---	---	.38	2.7	3.9
8	---	---	.74	1.35	3.8
9	---	---	.61	1.6	3.1
10	---	---	.43	2.3	4.4
11	---	---	.55	1.8	5.6

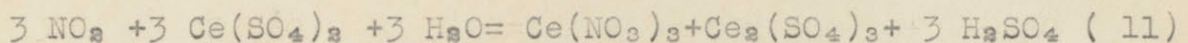
APPENDIX F.

ANALYSIS METHODS.

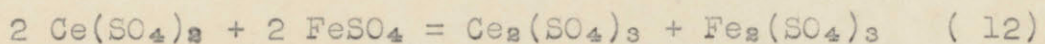
1. Liquid Analysis

A. Nitric Acid.

The nitric acid was analyzed for its NO_2 content by the use of $\text{Ce}(\text{SO}_4)_2$ in 60 % sulphuric acid. The acid was poured into an excess of $\text{Ce}(\text{SO}_4)_2$ and allowed to stand for several minutes. The sulphuric acid probably holds the nitrogen dioxide, forming nitrosylsulphuric acid, until the cerium can oxidize the NO_2 according to the following equation:



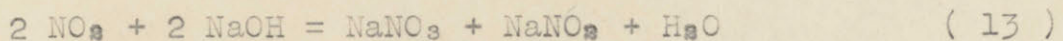
The excess $\text{Ce}(\text{SO}_4)_2$ was then titrated to an excess of FeSO_4 , according to the reaction:



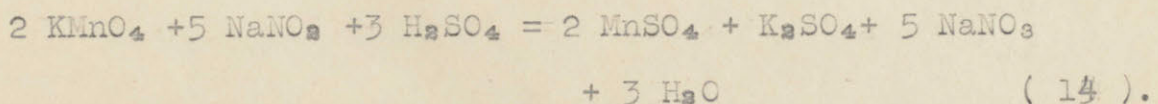
using ortho phenanthroline ferrous sulphate indicator.

B. Caustic Solutions.

Nitrogen dioxide is absorbed in sodium hydroxide solutions and reacts according to the equation:



forming the nitrate and the nitrite. The nitrite content is found by first acidifying with sulphuric acid, while cooling, and then titrating with KMnO_4 . The reaction is as follows:



2. Gas Analysis:

A known volume of gas can be analyzed for its nitrogen dioxide content by the same method used to analyze acids. The $\text{Ce}(\text{SO}_4)_2$ solution is added to the gas, the container sealed and then shaken for several minutes. The gas should now be completely colorless. The solution is washed out, diluted, and the excess $\text{Ce}(\text{SO}_4)_2$ titrated with FeSO_4 .

APPENDIX G.

SAMPLE CALCULATIONS.

1. Sample Calculation of Results.

Run No. 1.

Material balance check.

$$\begin{aligned} \text{NO}_2 \text{ lost from gas} &= \frac{1.9 \times 60 (Y_{\text{ent.}} - Y_{\text{leav.}})}{359 \times \frac{293}{273} \times \frac{760}{765}} \\ &= .297 (.0272 - .0050) \\ &= \underline{.0066} \text{ Lb.Mol. NO}_2 \text{/Hr.} \end{aligned}$$

NO₂ gained by liquid

$$\begin{aligned} &= 7.2 \times \frac{60}{454} (7.95 - .55) \\ &= \underline{.0070} \text{ Lb.Mol. NO}_2 \text{/ Hr.} \end{aligned}$$

Correction for material balance,

$$60 \times .0496 (.0272 - Y_{\text{leav.}}) = .0070$$

$$Y_{\text{leav.}} = \underline{.0036}$$

$$\begin{aligned} \text{N.T.U.} &= \frac{Y_{\text{ent.}} - Y_{\text{leav.}}}{(Y - Y^*)_{\text{l.m.}}} & \text{Use } Y_{\text{ent.}}^* &= .0021 \\ & & Y_{\text{leav.}}^* &= .0251 \\ &= \frac{.0236}{(.0272 - .0251) - (.0036 - .0021)} \\ & \ln \frac{.0272 - .0251}{.0036 - .0021} \end{aligned}$$

$$= \underline{13.2}$$

$$\text{H.T.U.} = 12/\text{N.T.U.}$$

$$= 12/13.2 = \underline{.91} \text{ in.}$$

$$\begin{aligned}
 K_Y a &= \frac{G}{S1} \quad (\text{N.T.U.}) \\
 &= \frac{.297}{.29 \times 1} \quad (13.2) \\
 &= 135 \text{ Lb.Mol.NO}_2/\text{Hr. Cu.Ft. (Y)}.
 \end{aligned}$$

Calculation of Y^* used in above .

at 15°C., 23 N. acid, s.g. = 1.49

$$Y_{\text{leav.}}^* = ?$$

$$\frac{7.95 \times 1000 \times 46}{1000 \times 10} \div 1490 + \text{above} \times 100 = 2.41 \text{ wt.}\% \text{ NO}_2$$

from Figure III, $P_{\text{NO}_2} = 18.8 \text{ mms.}$

$$\frac{18.8}{765 - 18.8} = .0251 = Y_{\text{leav.}}^*$$

NOTE:

Data used to find Y^* is not same as in run 1.

2. Calculation of acid analysis.

10 cc acid sample. Add 50 cc of 0.1 N $\text{Ce}(\text{SO}_4)_2$.

FeSO_4 titration used 20 cc FeSO_4 (.1 Normal).

10 X 1.49 = 14.9 gms acid

50 X .1 = 5 m.e. $\text{Ce}(\text{SO}_4)_2$ added

20 X .1 = 2 m.e. FeSO_4 used

3 m.e. NO_2 present.

3 X $\frac{46}{1000} = .138$ grams NO_2

$\frac{.138}{14.9} \times 100 = .91 \%$ NO_2

3. Calculation of caustic analysis

10 cc. caustic sample. acidify, titrate, takes

20 cc. of 0.1 N KMnO_4

$20 \times .1 = 2$ m.e. of NO_2 present.

$2 \times 46/1000 = .92$ grams NO_2 / 10 cc. caustic.

4. Calculation of gas analysis

volume of flask is 1040 ccms., Barom. = 29.5 inches,

temp = 23 ° C., Add 20 cc. of 0.087 N. $\text{Ce}(\text{SO}_4)_2$,

titration took 3.15 cc. of 0.126 N. FeSO_4 .

$$\frac{22.4 \times 29.9 \times 296}{29.5 \times 273} = 24.4 \text{ liters/gm./mol.}$$

$$\frac{1040}{24400} = .0427 \text{ gm. mols of gas}$$

in flask.

$$\begin{aligned} \text{m.e. NO}_2 &= 20 \times .087 - 3.15 \times .126 \\ &= 1.34 \text{ m.e. NO}_2. \end{aligned}$$

$$\frac{.00134}{.0427 - .00134} = .0324 = Y \quad (\text{Mol/Mol.})$$

APPENDIX H.

NOMENCLATURE.

a = Interfacial surface per unit volume, sq.ft./cu.ft..

G = Rate of flow of gas, Lb. Mol./Hr. Sq.Ft.

h = Height of mercury column in cms.

H.T.U. = Height of Transfer Unit in feet or inches.

k_L = Liquid film transfer coefficient, in Lb. Mol./
Hr. Sq.Ft. (driving force in mols/mol.sol.free liqd)

k_Y = Gas film transfer coefficient, in Lb. Mol./ Hr.
sq.ft. (driving force in Y).

K_Y = Overall transfer coefficient, units same as k_Y .

L = Liquid rate of flow , Lb. Mol./Hr. Sq.Ft.

l = Packed height of tower.

N = Amount of matter transferred.

N.T.U. = Number of Transfer Units.

P = Partial pressure in mms. Hg.

S = Cross sectional area of tower in sq. ft.

θ = Time

V = Volumetric rate of flow of gas in cu.ft./hr.

Y = Concentration of gas, expressed as Mols./Mol.
sol. free. gas).

Y^* = Concentration in gas in equilibrium with liquid, units
same as above.

Y_1 = Y at interface between gas and liquid.

APPENDIX I.

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