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Partial Pressures of N-dimethylnitrosamine Over an Alkaline Solution

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El Segundo, Calif. 90245

22 March 1976

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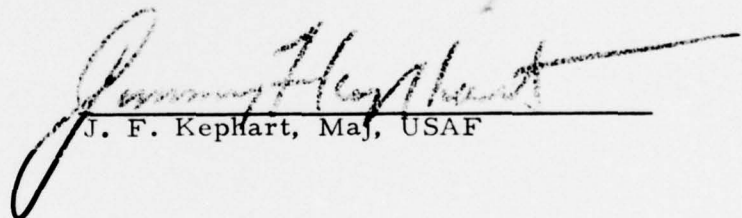
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This report has been reviewed by the Office of Information and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

Approved


J. F. Kephart, Maj, USAF

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

FOR THE COMMANDER



PREFACE

The author is indebted to Mr. A. Pallos for analyzing the condensed vapors by GC-mass spectrometry, and Mr. R. Beisel for preparing the solutions. Discussions with Dr. N. A. Gokcen were very helpful in interpretation of the results.

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I. INTRODUCTION

In recent years interest in nitrosamines has been heightened by the observation that they are usually carcinogenic to animals.^{1,2} N-dimethylnitrosamine, NDMA, is of special interest because it has been found in foods, in soil, and in some industrial waste solutions.³⁻⁵ Contamination by nitrosamines may present far-reaching biological and environmental hazards. In the storage or disposal of waste solutions containing NDMA, it is necessary to know the partial pressure of NDMA in order to determine the level of contamination to the environment. There are no data on the partial pressure of NDMA. In this investigation, the partial pressures of NDMA over an alkaline solution containing various amounts of NDMA were determined from 0 to 40°C. The composition of the alkaline solution was chosen to approximate that of an existing industrial waste solution. The removal of NDMA from solutions by gas-bubbling was also investigated.

¹J. H. Weisburger and E. K. Weisburger, "Chemicals as Causes of Cancer," Chem. Eng. News, **44**, 124 (Feb. 1966).

²P. N. Magee and J. M. Barnes, "The Production of Malignant Primary Hepatic Tumors in the Rat by Feeding Dimethylnitrosamine," Br. J. Cancer, **10**, 114 (1956).

³N. P. Sen, D. C. Smith, L. Schwinghamer, and B. Howsman, "Formation of Nitrosamines in Nitrite-Treated Fish," Can. Inst. Food Technol. J., **3**, 66 (1970).

⁴A. Ayanaba, W. Verstraete, and M. Alexander, "Formation of Dimethylnitrosamine, a Carcinogen and Mutagen, in Soils Treated with Nitrogen Compounds," Soil Science Soc. Amer. Proc., **37**, 565 (1973).

⁵R. L. Tate and M. Alexander, "Stability of Nitrosamine in Samples of Lake Water, Soil, and Sewage," J. Nat. Cancer Inst., **54**, 327 (1975).

II. EXPERIMENTAL PROCEDURE

The equilibrium partial pressure of NDMA over the alkaline waste solution is determined by using the static method and the gas-bubbling method. The static total vapor pressure, P_{Total} , of the alkaline waste solution is measured by the conventional static method described in an earlier report.⁶ The total pressure is the sum of the partial pressures of NDMA, p_{NDMA} ; and of H_2O , $p_{\text{H}_2\text{O}}$; therefore,

$$P_{\text{Total}} = Y_{\text{NDMA}} P_{\text{Total}} + Y_{\text{H}_2\text{O}} P_{\text{Total}} \quad (1)$$

where Y_{NDMA} and $Y_{\text{H}_2\text{O}}$ are the mole fractions of NDMA and H_2O in the vapor respectively. Contribution to the total pressure by NaOH , NaNO_3 , and NaNO_2 is negligibly small, below 100°C .

In the gas-bubbling method, a measured volume of inert gas is passed very slowly through the solution at a fixed temperature. The inert gas contains the equilibrium concentration of vapor after passing through the solution. The amount of liquid vaporized is obtained by condensing the vapor from the gas stream in a weighed trap. Since more than one component of the solution is volatile, the condensed vapor is analyzed before the partial pressure of each component can be determined. The partial pressure of a component i , p_i , is calculated from

$$p_i = \frac{g_i}{M_i} \frac{RT}{V} \quad (2)$$

⁶ E. T. Chang, Vapor Pressure of N-Nitrosodimethylamine, Report SAMSO-TR-75-306, The Aerospace Corporation, El Segundo, Calif., 15 January 1976.

where R is the gas constant; T , the temperature; V , the total volume of saturated gas; M_i , molecular weight of component i ; and g_i , grams of condensed vapor of component i .

The apparatus used for the gas-bubbling method of vapor pressure measurement, shown in Figure 1, consisted of a cylinder of N_2 gas, A; a flow regulator, B; a saturator, C; a thermostated bath, D; a heating tape, E; a small removable trap, F; a wet test meter, G; and three stopcocks, H, I, and J. The saturator, C, contained a bubbler for the incoming inert gas stream and a side arm exit for the saturated gas. The saturator contained 130 cm^3 of solution. The small trap, F, had a capacity of about 1 cm^3 and it was cooled with liquid N_2 .

The general procedure for collecting a condensed vapor sample was as follows: The flow of N_2 gas was adjusted to $35\text{ cm}^3/\text{min}$; 120 cm^3 of solution was charged into the saturator; the thermostated bath was controlled at a desired temperature and the solution was allowed to reach thermal equilibrium with the bath temperature; then trap F was cooled with liquid N_2 , the heating tape E was turned on, and stopcocks H, I, and J were opened to start the N_2 gas flow. When about 0.1 cm^3 of vapor was condensed in trap F, stopcocks H, I, and J were closed. The volume of N_2 gas passed through the solution was obtained from the wet-test meter reading and the amount of vapor condensed was determined by weighing.

The condensed vapor was analyzed by GC-mass spectrometry to determine the concentration of NDMA. The partial pressure of NDMA was calculated by Eq. (1).

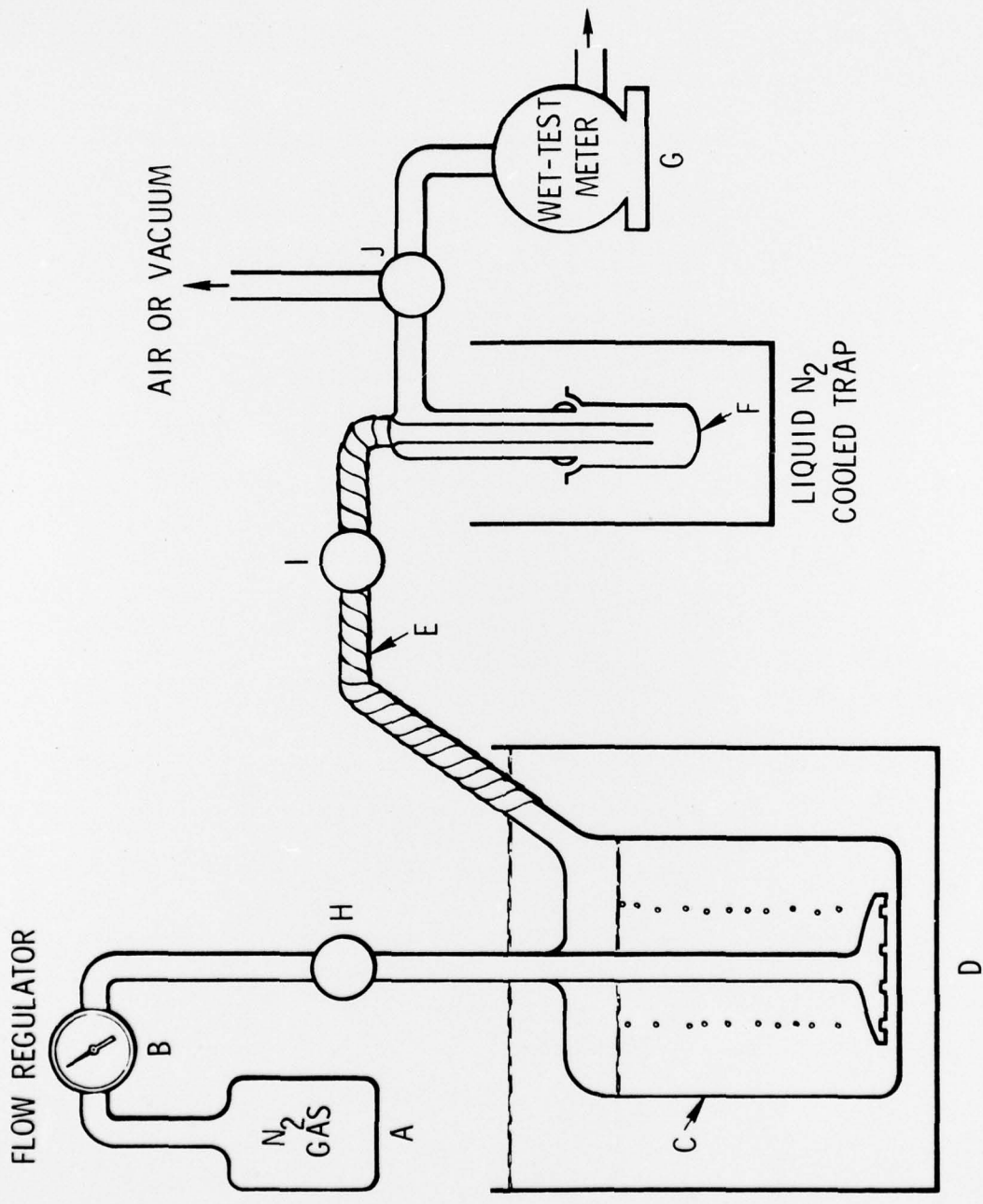


Figure 1. Gas-Bubbling Apparatus

III. RESULTS

The equilibrium vapor pressure of an alkaline solution containing 15 wt% NaOH, 7 wt% NaNO₃, 6 wt% NaNO₂, 72 wt% H₂O, and 317 ppm NDMA, determined by the static method at 0, 10, 25, and 40°C, are listed in Table 1.

Table 1. Equilibrium Vapor Pressure of an Alkaline Solution Containing 317 ppm NDMA, Static Method

t, °C	P _{Total} , mmHg
0	3.18 ± 0.01
10	6.24 ± 0.05
25	16.65 ± 0.03
40	39.60 ± 0.05

The equilibrium vapors from the same alkaline solution containing various amounts of NDMA were collected by the gas-bubbling method at 0, 10, 25, and 40°C. Results of the gas-bubbling experiments at various temperatures are listed in Table 2.

Table 2. Results of Gas-Bubbling Experiments

NDMA in Solution ppm	Liters of N ₂ Gas and Grams of Condensed Vapor*							
	0°C		10°C		25°C		40°C	
	liters	grams	liters	grams	liters	grams	liters	grams
7	16.99	0.100			6.23	0.100	3.40	0.108
78	14.75	0.051			8.24	0.103	2.70	0.100
194	28.88	0.091	12.18	0.054	5.95	0.099	2.83	0.117
300	56.63	0.163	22.65	0.111	13.41	0.205	3.11	0.120

* Within ± 0.03 liter and ± 0.001 gram

The condensed vapors were analyzed by GC-mass spectrometry and the results are presented in Table 3.

Table 3. Concentration of NDMA in Condensed Vapor

ppm NDMA in Solution	ppm NDMA in Condensed Vapor			
	at 0°C	at 10°C	at 25°C	at 40°C
7	84 ± 4	-	153 ± 18	85 ± 9
78	1200 ± 200	-	1075 ± 75	2325 ± 175
194	4650 ± 100	3900 ± 350	5400 ± 600	4500 ± 150
300	8400 ± 400	8100 ± 400	6800 ± 200	6000 ± 600

The total pressures over each solution at various temperatures, as determined by the composition and the amount of condensed vapors and calculated by Eq. (2) are presented in Table 4. These values are in fair agreement with those determined by the static method and listed in Table 1.

Table 4. Equilibrium Vapor Pressures of Alkaline Solutions Containing Various Amounts of NDMA, Gas-Bubbling Method

t, °C	P_{Total} , mmHg*			
	300 ppm NDMA Solution	194 ppm NDMA Solution	78 ppm NDMA Solution	7 ppm NDMA Solution
0	2.95	3.24	3.56	6.00
10	4.98	4.50	-	-
25	15.16	16.77	12.67	16.14
40	37.47	40.12	36.10	31.33

* Average discrepancy with static method is 11%.

The partial pressure of NDMA, p_{NDMA} , over the alkaline solution is calculated from $p_{\text{NDMA}} = Y_{\text{NDMA}} P_{\text{Total}}$, where Y_{NDMA} is the mole fraction of NDMA in the vapor, and P_{Total} the total vapor pressure of the alkaline solution determined by the static method. The mole fractions of NDMA in the liquid and vapor phases, and the equilibrium partial pressures of NDMA at various temperatures are presented in Table 5.

Table 5. Partial Pressure of NDMA Over Solutions of Various Compositions at Various Temperatures

Temp. °C	ppm NDMA in Solution	Mole Fraction of NDMA in Solution $10^5 X_{\text{NDMA}}$	Mole Fraction of NDMA in Vapor $10^5 Y_{\text{NDMA}}$	Partial Pressure of NDMA P_{NDMA} 10^3 mmHg
0	7.4	0.22	2.04	0.07
	78	2.32	29.2	0.93
	192	5.69	113	3.61
	312	9.27	205	6.53
10	190	5.63	95.1	5.94
	304	9.03	198	12.4
25	7.5	0.22	3.72	0.62
	79	2.34	26.1	4.35
	198	5.89	132	21.9
	296	8.79	166	27.7
40	7.4	0.22	2.07	0.82
	77	2.30	56.6	22.4
	195	5.79	110	43.5
	288	8.56	147	58.0

IV. CORRELATION OF DATA

The foregoing data can be correlated by simple thermodynamic relationships. The vaporization of NDMA can be written as a simple reaction; i. e.



The equilibrium constant K_{NDMA} for this reaction is

$$K_{\text{NDMA}} = \frac{p_{\text{NDMA}}}{X_{\text{NDMA}}} \quad (4)$$

where p_{NDMA} is the partial pressure of NDMA in atm in the vapor and X_{NDMA} is the mole fraction of NDMA in the solution. At low concentrations of NDMA, i. e. $X_{\text{NDMA}} \rightarrow 0$, the solution obeys Henry's law so that $p_{\text{NDMA}}/X_{\text{NDMA}}$ is a constant. The equilibrium constants, K_{NDMA} obtained by the average of the values* of $p_{\text{NDMA}}/X_{\text{NDMA}}$, are 0.0762, 0.1593, 0.3829, and 1.0545 for 0, 10, 25, and 40°C, respectively. A plot of $\log_{10} K_{\text{NDMA}}$ versus $10^3/T$ in K^{-1} for NDMA is shown in Figure 2. The linear equation representing the data, obtained by the method of least squares to within $\pm 10\%$, is

$$\log_{10} K_{\text{NDMA}} = \log_{10} \frac{p_{\text{NDMA}}(\text{atm})}{X_{\text{NDMA}}} = \frac{-2413}{T} + 7.71 \quad (5)$$

*Only values for the 78 ppm, 194 ppm, and 300 ppm NDMA solutions are averaged to obtain the constants. Values for the 7 ppm NDMA are omitted due to large uncertainties.

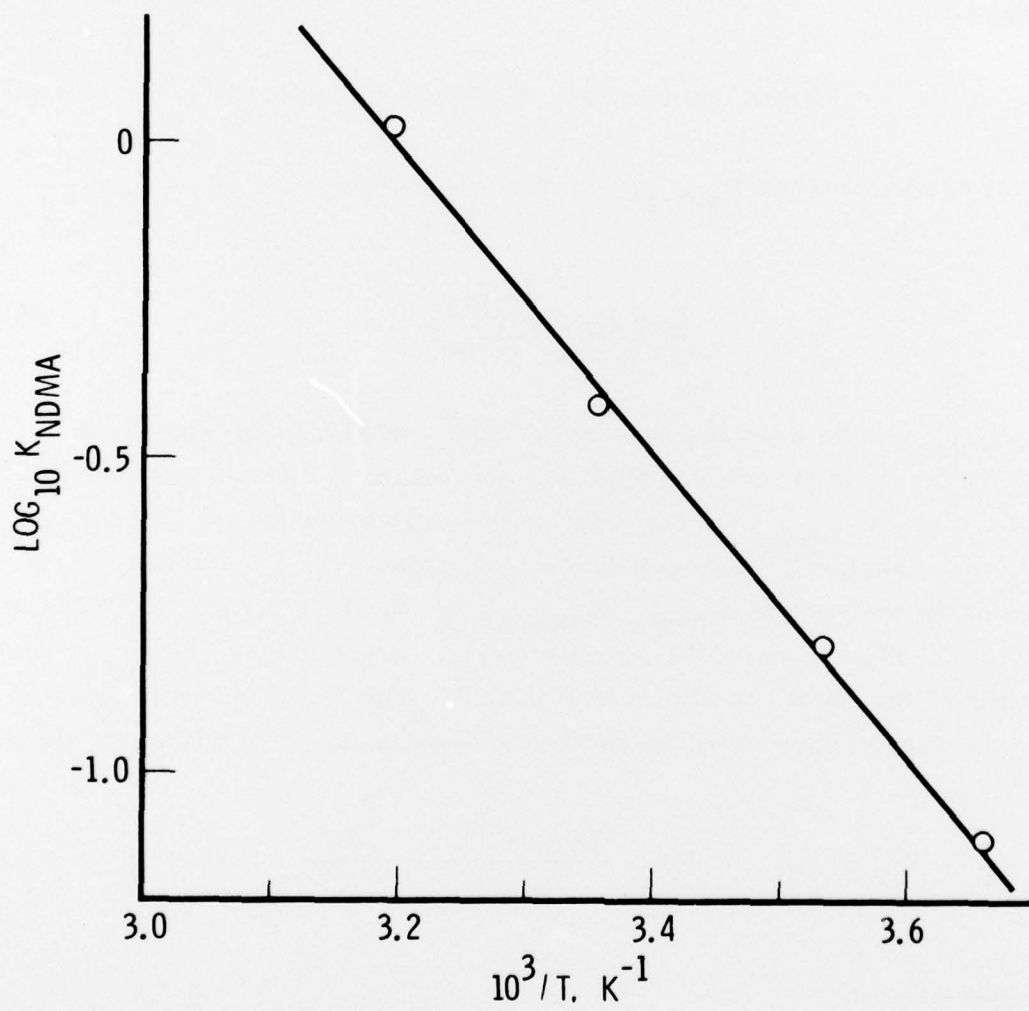


Figure 2. Equilibrium Constants of NDMA over an Alkaline Solution at Various Temperatures

The standard Gibbs energy change, ΔG° for reaction in Eq. (3), is

$$\Delta G^\circ = -RT \ln K_{\text{NDMA}} \quad (6)$$

Substitution of Eq. (5) in Eq. (6) yields

$$\Delta G^\circ = 11,041 - 35.28 T \quad (7)$$

Comparison with the definitional equation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ gives $\Delta H^\circ = 11,041$ cal/mole and $\Delta S^\circ = 35.28$ cal/mole K, where ΔH° and ΔS° are the standard enthalpy and entropy of vaporization, respectively.

V. REMOVAL OF NDMA BY GAS-BUBBLING

Removal of NDMA from the alkaline waste solution by bubbling a dry N_2 gas stream through the solution is now considered. The amounts of water and NDMA that can be vaporized for a given reduction of NDMA in solution can be calculated from the equilibrium partial pressures of NDMA and H_2O over the solution as follows:

$$\frac{-dm_{\text{NDMA}}}{dt} = m_{\text{gas}} Y_{\text{NDMA}} \quad (8)$$

where $-dm_{\text{NDMA}}/dt$ is the number of moles of NDMA removed per unit of time; m_{gas} , moles of gas flow per unit time; and Y_{NDMA} , mole fraction of NDMA in the gas stream. From $Y_{\text{NDMA}} = p_{\text{NDMA}}/P_{\text{Total}}$, for 1 atm of total pressure, it is evident that $Y_{\text{NDMA}} = p_{\text{NDMA}}$. Since $K_{\text{NDMA}} = p_{\text{NDMA}}/X_{\text{NDMA}}$, then $Y_{\text{NDMA}} = p_{\text{NDMA}} = K_{\text{NDMA}} X_{\text{NDMA}}$. On the basis of one mole of solution as the starting material, m_{NDMA} is equal to X_{NDMA} . Equation (8) now becomes

$$\frac{-dX_{\text{NDMA}}}{dt} = m_{\text{gas}} K_{\text{NDMA}} X_{\text{NDMA}} \quad (9)$$

and rearrangement gives

$$\frac{-dX_{\text{NDMA}}}{X_{\text{NDMA}}} = m_{\text{gas}} K_{\text{NDMA}} dt \quad (10)$$

Integration of Eq. (10) yields

$$\ln \frac{X_{\text{NDMA}}^i}{X_{\text{NDMA}}^f} = (m_{\text{gas}} t) K_{\text{NDMA}} \quad (11)$$

where X_{NDMA}^i and X_{NDMA}^f are the initial and final mole fractions of NDMA in the solution. Likewise for H_2O vapor,

$$\ln \frac{X_{\text{H}_2\text{O}}^i}{X_{\text{H}_2\text{O}}^f} = (m_{\text{gas}} t) K_{\text{H}_2\text{O}} \quad (12)$$

The quantity $(m_{\text{gas}} t)$ for a given reduction in NDMA concentration is determined by Eq. (11). The moles of dry N_2 gas is given by $Y_{\text{N}_2} (m_{\text{gas}} t)$, where Y_{N_2} is the mole fraction of N_2 in the gas stream leaving the solution. Then $X_{\text{H}_2\text{O}}^f$, the final mole fraction of H_2O in the solution is calculated by substituting the value for $(m_{\text{gas}} t)$ in Eq. (12). The amount of H_2O evaporated with the NDMA is the difference between $X_{\text{H}_2\text{O}}^i$ and $X_{\text{H}_2\text{O}}^f$. The calculation of evaporated water requires the values of the equilibrium constant $K_{\text{H}_2\text{O}}$ for H_2O that are calculated from the vapor pressure measurements in Table 1. These values for $K_{\text{H}_2\text{O}}$ are 4.89×10^{-3} and 5.92×10^{-2} at 0 and 40°C respectively. The moles of dry N_2 gas that are required to be bubbled through the solution and the moles of H_2O that are evaporated from a solution for a 50% and a 95% reduction in NDMA concentration in the solution have been calculated by Eqs. (11) and (12) and listed in Table 6. It was found that for 50% and 95% reduction in NDMA concentration, large amounts of H_2O are removed. Therefore, the fixed values used for $K_{\text{H}_2\text{O}}$ and K_{NDMA} for a given temperature may actually vary due to the large changes in the composition of solution because the activities of NDMA and H_2O are no longer constants. Extensive measurements are therefore necessary to determine the effects of composition on K_{NDMA} and $K_{\text{H}_2\text{O}}$. However, the foregoing calculations give reliable orders of magnitude of the removal of NDMA and H_2O .

Table 6. Removal of NDMA and H₂O From Alkaline Solution by Gas-Bubbling at 0 and 40°C

Solution Temp. t, °C	% NDMA* Removed	Initial Mole Fraction of H ₂ O in Solution $X_{H_2O}^i$	Moles of Dry N ₂ Gas per Mole of Solution	Final Mole Fraction of H ₂ O in Solution $X_{H_2O}^f$	% H ₂ O* Removed
0	50	0.88	8.81	0.64	26.9
40	50	0.88	0.63	0.66	25.4
0	95	0.88	38.1	0.32	63.3
40	95	0.88	2.69	0.35	61.0

* Based on initial amounts of NDMA and H₂O in solution.

VI. CONCLUSION

The equilibrium partial pressure of NDMA, over an alkaline solution (15 wt% NaOH, 7 wt% NaNO₃, 6 wt% NaNO₂, and 72 wt% H₂O) containing various amounts of NDMA can be determined to within $\pm 10\%$ by Eq. (5) over the temperature range from 0 to 40°C. However, the variation of the partial pressure of NDMA with the alkaline concentration in solution should be investigated in order to obtain a more realistic correlation.

The removal of NDMA from alkaline solutions by gas-bubbling is not practical because the process also involves the evaporation of excessively large amounts of H₂O from the solutions. Bubbling moist N₂ gas will simply prevent the evaporation of H₂O from the solution corresponding to the moisture contents of N₂ without improving the removal of NDMA. However, the process of bubbling N₂ can separate large amounts of NDMA from an alkaline solution into a neutral solution where treatment by other chemical means or photolysis is much more effective than in the alkaline solutions.