[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH DAKOTA]

Vapor Density of Nitrogen Tetroxide over Carbon Tetrachloride Solutions by a Colorimetric Method

BY E. D. COON

During the progress of some measurements upon the heat of solution of nitrogen tetroxide in carbon tetrachloride it became necessary to make corrections for the effect of the nitrogen tetroxide which remained undissolved in the vapor above the solution. The nitrogen tetroxide was introduced into the solution as a liquid, but a part of this liquid evaporated into the free space above the solution and in the vapor phase partially dissociated into nitrogen dioxide. Each of these processes, evaporation and dissociation, absorbs heat, hence the necessity for correction.

A constant difficulty encountered by the usual methods of withdrawing some of the vapor for analysis, as by bubbling a known volume of air through the solution, is that with the removal of nitrogen tetroxide vapor from above the solution, more leaves the solution, thus continually altering the concentration. The following colorimetric method being a static one does not meet this difficulty.

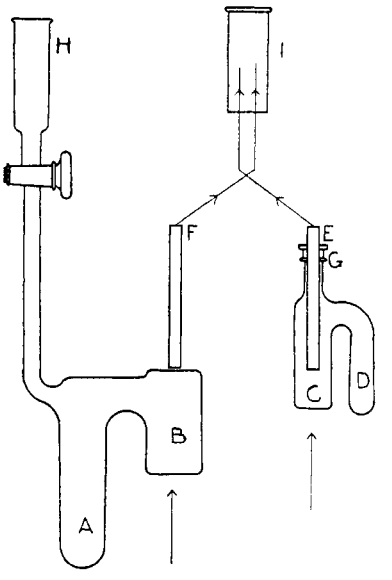

Fig. 1.

Materials.—The nitrogen tetroxide was prepared by heating lead nitrate and condensing the gas in a flask containing phosphorus pentoxide, from which it was distilled after several days into small glass capsules, in the manner described by Daniels, Mathews and Williams.[1]

The carbon tetrachloride was purified by refluxing for two hours with potassium dichromate and sulfuric acid and fractionating, retaining the portion boiling between 75.18 and 75.20°.

Apparatus and Method.—The apparatus, shown in Fig. 1, consists of two vessels so arranged that they may be observed in a Bausch and Lomb colorimeter. The vessel on the left has two chambers, designated A and B. Into A is placed the solution of nitrogen tetroxide. To facilitate the equilibrium between the solution and its vapor in B, the vessel is evacuated before the solution is introduced. The total volume of this vessel was 75 cc.

The vessel on the right also consists of two chambers. Liquid nitrogen tetroxide is placed in it and allowed to boil (boiling point 21°) until most of the air has been carried out by escaping vapor. The glass plunger E of the colorimeter is put in place and made gas tight by the packing gland G. Side D is cooled in an ice-bath and the nitrogen tetroxide condensed in it. Upon warming, side C contains only vapors of nitrogen tetroxide and nitrogen dioxide at a pressure determined by the temperature. This vessel is now fastened securely in the movable rack of the colorimeter.

Experimental

The vessel CD was filled as described. Vessel AB was evacuated, weighed and liquid nitrogen tetroxide was placed in H. The stopcock was opened cautiously until most of the liquid was drawn into AB, but closed in time to avoid admitting any air. The remaining liquid in H was dried out by a stream of air and the vessel and contents reweighed. The carbon tetrachloride was admitted in the same manner and its weight determined. After assembly, the whole apparatus was submerged in a large water thermostat and kept constant at 25 ± 0.01°. After twenty to thirty minutes the colorimeter readings were made.

The depth of vapor viewed in B is constant but in C the depth is variable by moving vessel CD up or down, the plunger E remaining stationary. The concentration of nitrogen dioxide vapor in B is matched with that in C. Thus

$$\frac{\text{depth C}}{\text{depth B}} = \frac{\text{concentration of } NO_2 \text{ in B}}{\text{concentration of } NO_2 \text{ in C}}.$$

At 25° the concentration of nitrogen dioxide is 0.01275 mole per liter; the concentration of nitrogen tetroxide is 0.03593 mole per liter. The total quantity of vapor, calculated as undissociated nitrogen tetroxide, is 0.04230 mole per liter. These values are obtained by extrapolating the data of Verhoek and Daniels.[2] Practically the same values are obtained directly from Scheffer and Treub.[3]

The Data.—The results of this investigation are presented in the table. The solutions were pre-

(1) Daniels, Mathews and Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., Inc., New York, 1920, p. 115.

(2) Verhoek and Daniels, THIS JOURNAL, **53**, 1250 (1931).

(3) Scheffer and Treub, *Z. physik. Chem.*, **81**, 309 (1912).

TABLE I

$n_{N_2O_4}$	n_{CCl_4}	V	$\frac{n_{CCl_4}}{n_{N_2O_4}}$	Colorimeter	C_{NO_2}(gas)	α	$C_{N_2O_4}$(gas)	$N_{N_2O_4}$	k	N_{NO_2}	k'
.....	.....	...	0.00	100.0	0.01275	0.1508	0.03593	.....	....	.....	..
0.01850	0.01008	2.11	.544	84.0	.01071	.188	.02314	0.6442	0.0359	0.003786	2.82
.01277	.00910	1.66	.71	77.5	.00988	.205	.01916	.5810	.0330	.003654	2.70
.01900	.0200	3.09	1.05	73.2	.00933	.217	.01677	.4847	.0346	.003402	2.74
.01920	.02995	4.06	1.56	68.7	.00876	.230	.01457	.3885	.0375	.003112	2.81
.01270	.02194	2.89	1.73	68.9	.00878	.239	.01471	.3646	.0403	.003029	2.89
.01955	.0503	6.05	2.572	60.3	.00769	.256	.01110	.2781	.0399	.002696	2.85
.01372	.0590	6.52	4.30	53.7	.00685	.286	.00858	.1873	.0458	.002253	3.04
.01200	.0621	6.71	5.17	50.1	.00639	.300	.00735	.1607	.0457	.002098	3.04
.01386	.0795	8.50	5.73	48.9	.00623	.307	.00708	.1473	.0480	.002015	3.09
.00530	.0308	3.28	5.81	47.6	.00607	.316	.00661	.1457	.0454	.002002	3.03
.00805	.04945	5.26	6.14	46.4	.00592	.319	.00634	.1388	.0456	.001963	3.02
.00550	.0513	5.28	9.327	39.1	.00498	.358	.00446	.09595	.0465	.001644	3.00
.00570	.0821	8.25	14.40	32.8	.00418	.402	.00311	.06419	.0484	.001354	3.09
.00570	.1027	10.25	18.00	30.45	.00388	.421	.00266	.05192	.0512	.001223	3.17
.00387	.0742	7.38	19.16	29.5	.00376	.427	.00252	.04940	.0510	.001187	3.17
.00572	.1230	12.15	21.53	27.65	.00352	.439	.00224	.04385	.0511	.001122	3.14
.00395	.1078	10.61	27.28	24.9	.00317	.469	.00181	.03483	.0520	.001004	3.06
.00168	.0776	7.56	46.20	21.75	.00277	.506	.00136	.02079	.0654	.000779	3.55

pared by weighing into vessel AB the number of moles of nitrogen tetroxide and of carbon tetrachloride shown in columns one and two. The volume of the resulting solution in milliliters is in column three and its mole fraction in column four. The readings of the colorimeter give the depth of vapor in vessel C; an arbitrary depth of 100 is required when pure nitrogen tetroxide is in vessel A.

The whole system to be considered here may be represented as

$$\begin{array}{ccc} & \overset{(a)}{\rightleftharpoons} & \\ N_2O_4 & & 2NO_2(\text{gas}) \\ (c)\downarrow\uparrow & & \downarrow\uparrow(d) \\ N_2O_4 & \underset{(b)}{\rightleftharpoons} & 2NO_2(\text{in } CCl_4 \text{ solution}) \end{array}$$

The constant for the dissociation in the gas phase reaction (a) is given by Verhoek and Daniels[2] as $K_a = 0.1426 - (0.7588 \times C^0_{N_2O_4})$ where $C^0_{N_2O_4}$ is the idealized concentration in moles per liter of nitrogen tetroxide, assuming no dissociation. The values given for α are obtained from this constant $K_a = 4\alpha^2P/(1-\alpha^2)$ in which P is the combined pressure of nitrogen dioxide and nitrogen tetroxide at 25°.

For the dissociation in carbon tetrachloride solution, reaction (b) above, the constant $K_b = 4x^2/(a-x^2) = 3.01 \times 10^{-4}$ moles per liter.[4]

The concentration of nitrogen dioxide in the vapor above the solution, C_{NO_2}(gas), (see table and equilibrium (d) above), has been measured colorimetrically, and $C_{N_2O_4}$(gas) calculated. The constants k and k' are obtained in the manner noted below.

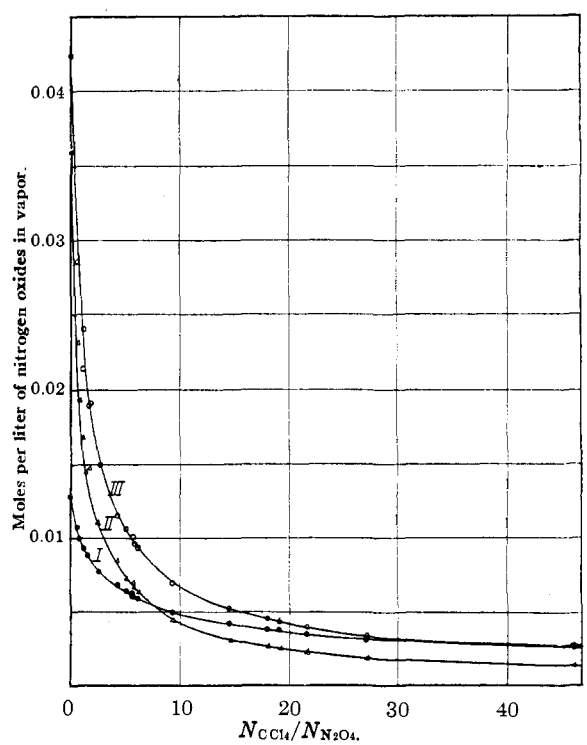

Fig. 2.—Concentration of nitrogen oxide vapors over carbon tetrachloride solutions: Curve I is nitrogen dioxide; II is nitrogen tetroxide; III is the total vapor calculated as undissociated nitrogen tetroxide.

The data and calculations for the first experiment are given to illustrate the method. The

(4) From unpublished data of Holmes and Daniels, University of Wisconsin.

weight of nitrogen tetroxide introduced into vessel AB was 0.01850 mole, followed by 0.01008 mole of carbon tetrachloride, giving a volume V of 2.11 ml., and containing 8.768 moles per liter of nitrogen tetroxide. The latter is the value for a in the expression $K_b = 4x^2/(a - x^2)$. This expression when solved for $x = 0.008674\sqrt{a}$. In this first experiment x equals 0.02568 mole of nitrogen tetroxide dissociated into nitrogen dioxide per liter of carbon tetrachloride solution.

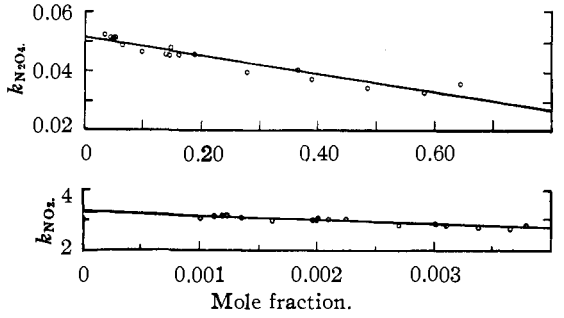

Fig. 3.

Consecutively, values for $(a-x)\ V$, $(a + x)\ V$ and $2xV$ are calculated, which are, respectively, the $N_{N_2O_4}$, $N_{N_2O_4} + N_{NO_2}$ and N_{NO_2} of the following equations. The values for N_{CCl_4} and C_{NO_2} are given in the table. Substituting into the following equations

$$C_{N_2O_4} = k \frac{N_{N_2O_4}}{N_{NO_2} + N_{N_2O_4} + N_{CCl_4}}$$

and

$$C_{NO_2} = k' \frac{N_{NO_2}}{N_{NO_2} + N_{N_2O_4} + N_{CCl_4}}$$

k is found to be 0.0359 and k' is 2.82.

The two curves, Fig. 3, are reproduced by the following equations obtained by the method of least squares

$$k = 0.05102 - (0.03011 \times N_{N_2O_4})$$
$$k' = 3.271 - (134.25 \times N_{NO_2})$$

The fact that k and k' of the experimental data are so nearly constant indicates that nitrogen tetroxide and nitrogen dioxide form almost ideal solutions in carbon tetrachloride.

Summary

1. The vapor density of nitrogen dioxide over its solutions with carbon tetrachloride at 25° has been measured colorimetrically.

2. A colorimetric method which may be applied to any colored gas or vapor has been described.

3. The constants for solutions of nitrogen tetroxide and nitrogen dioxide with carbon tetrachloride have been calculated and the solutions have been found to be nearly ideal.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF YALE UNIVERSITY]

Solubility of Sodium and Potassium Chlorides in Corresponding Hydroxide Solutions at 25°

BY GÖSTA ÅKERLÖF AND OLIVER SHORT

Introduction

The solubilities of sodium and potassium hydroxide in water at 25° are about 28.3 and 21.2 molal, respectively. The studies of Freeth, Antropoff, Marcau and Sommer[1] and others have shown that in the presence of the corresponding chlorides the latter form solid phases up to near the hydroxide saturation concentration in pure water. In view of this unusually large concentration range for the existence of the chloride solid phases their solubility curves have been determined in order to study the applicability of the general solubility equation previously suggested by one of us to the data obtained. It appears that within the ordinary experimental errors the solubility curves follow very closely the equation required.

(1) Freeth, *Phil. Trans. Roy. Soc.*, **A223**, 35 (1932); Antropoff, Marcau and Sommer, *Z. Elektrochem.*, **30**, 457 (1924).

Experimental Procedure

A detailed description may be omitted since previously used methods were followed without any essential variations. The hydroxides employed were analytical reagents that appeared to contain only very faint traces of alkali halides or sulfates. In the case of sodium hydroxide a practically carbonate-free solution was obtained by allowing the saturated liquid to stand undisturbed for several weeks until all suspended matter had settled out. To the stirred, saturated solution of potassium hydroxide were added appropriate