[CONTRIBUTION FROM THE JET PROPULSION LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Measurements on the Equilibrium between Hydrazine and Water in the Vapor Phase[1]

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A study was made of the equilibrium between hydrazine and water in the vapor phase by following the pressure change in a constant volume apparatus. The reaction was found to follow Equation (1) over the temperature range $5 < t < 90°$ and the pressure range $2 < p < 10$ mm. The thermodynamic constants obtained for Equation (1) are given in Equations (7)–(10).

I. Introduction

Several observations have been made which indicate that hydrazine and water unite to form definite compounds. Maxima and minima in the physical properties of hydrazine–water mixtures have been observed at close to equimolar concentrations of the components. For example, the melting-point diagram, which has been measured by both Semishin[2] and Mohr and Audrieth[2] shows two eutectics with a maximum at 50 mole per cent. N_2H_4. Similarly, the specific gravity and viscosity curves, as shown by Semishin and others, exhibit maxima at approximately 50 mole per cent. N_2H_4.[3] These phenomena have led to the belief that the compound hydrazine hydrate ($N_2H_4 \cdot H_2O$) exists in the liquid phase, however, whether or not other polyhydrates could also exist was uncertain.[4]

The only published work previously done on the composition of $N_2H_4 \cdot H_2O$ vapor appears to be the investigation of A. Scott[4] on vapor density measurements.[5] He observed that the molecular weight of $N_2H_4 \cdot H_2O$ at 98.8° and 366 mm. was 31.6 and that at 138° and 744.1 mm. it was just half the formula weight. These data are insufficient to permit the calculation of thermodynamic quantities except for the equilibrium constant at the one temperature, 98.8°. This value may be shown to be $K = 0.244$ atmosphere for the reaction as written in Equation (1).

Björkman[6] has made measurements on the vapor liquid equilibrium for the hydrazine–water system.[7] His data, however, were presented only in terms of over-all hydrazine content as determined by chemical analysis and no conclusions were drawn with regard to the dissociative equilibrium of $N_2H_4 \cdot H_2O$ in the liquid or vapor phase.

II. Experimental

1. **Materials.**—A sample of hydrazine uncontaminated with ammonia was carefully chosen for these tests. Quantitative analysis of this material showed that it consisted of 97.88 wt. % hydrazine and 2.12 wt. % water. Distilled water was then added to make solutions of three concentrations. The compositions as determined by analyses were

1. 21.55 mole % hydrazine, 78.45 mole % water
2. 35.20 mole % hydrazine, 64.80 mole % water
3. 53.60 mole % hydrazine, 46.40 mole % water

These samples were kept in an atmosphere of nitrogen in all-glass containers fitted with ground-glass stoppers.

2. **Apparatus and Procedure.**—An all-glass apparatus of constant volume was used for the study of the equilibrium constants for the dissociation of hydrazine hydrate to hydrazine and water in the vapor phase.

One drop of hydrazine–water solution was introduced into the flask and the mixture was frozen with liquid nitrogen. While the hydrazine–water mixture was kept in the frozen state, the flask and manometer were connected to the vacuum system.

After the system had been evacuated completely, the bulb containing the frozen mixture of hydrazine and water was disconnected from the vacuum system and then allowed to vaporize by replacing the liquid nitrogen bath surrounding the bulb with a water bath at approximately 35°. The bulb was then reconnected to the manometer and the pressure difference on the manometer noted.

The temperature was then systematically changed, and after sufficient time was allowed for equilibrium to obtain at each point, the pressure was recorded. At the end of each test the apparatus was allowed to return to room temperature, and the final pressure was noted. Thus it was possible to determine whether or not any thermal decomposition of the hydrazine to ammonia and nitrogen had taken place in the course of the test. Since both nitrogen and ammonia are non-condensable gases over the temperature and pressure ranges studied, and since the thermal decomposition reaction is irreversible, the absence of any measurable pressure increase at room temperature from the beginning to the end of the test was taken to indicate that the hydrazine had undergone no significant irreversible chemical change due to heat effects.

The thermostat temperature was held constant to ±0.3° as read by a Weston dial-type testing thermometer which had been calibrated with a standard mercury instrument. The manometer fluid was Octoil S, a vacuum-pump oil having very low vapor pressure and a density of 0.91101 g./cc. at 23.8°. A cathetometer was used for all the pressure readings taken. This instrument gave a precision in the pressure measurement of ±0.1 mm. of Octoil S, or about ±0.007 mm. of mercury.

The volume of the apparatus immersed in the thermostat was about 650 cc., whereas that remaining at room temperature was about 2 cc. Thus approximately 0.3% of the volume of gases was not at the thermostatic temperature upon which the calculations were based. This error was deemed negligible after tests utilizing pure distilled water failed to reveal any deviation from the perfect gas laws assuming the entire volume to be isothermal.

III. Analysis of Data

An estimate of the imperfection of the gases from their critical constants showed that deviations from ideality were entirely negligible under the conditions of these experiments. The total pres-

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[2] (a) V. I. Semishin, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 654 (1938); (b) P. H. Mohr and L. F. Audrieth, *J. Phys. Colloid Chem.*, **53**, 901 (1949).

[3] Th. Curtius, *Ber.*, **29**, 759 (1896).

[4] A. Scott, *J. Chem. Soc.*, **85**, 913 (1904).

[5] NOTE IN PROOF.—Since submission of this paper for publication, we have noticed a paper on this subject by L. V. Coulter, THIS JOURNAL, **73**, 3505 (1951). Using a similar apparatus, Coulter made measurements of *p vs. T* for the single composition $N_2H_4 \cdot H_2O$ near saturation in the temperature range 86–140° and concluded that no association occurs in the vapor. Considering his claimed pressure sensitivity of 0.2 mm. as compared to ours of 0.007 mm. and his higher temperatures, it is possible that this effect was not detected. Indeed, the fact that in three out of four of his experiments the observed molecular weights were 4% higher than theoretical indicates the possibility of association.

[6] A. Björkman, *Svensk Kem. Tid.*, **11**, 211 (1947).

[7] D. W. Scott, G. D. Oliver, M. E. Gross, W. N. Hubbard and H. M. Huffman, THIS JOURNAL, **71**, 2293 (1949).

sure P was therefore given by the equation of state for a perfect gas, $PV = nRT$, and the partial pressures of the constituents were given by Dalton's law.

Since no evidence of thermal decomposition of hydrazine to ammonia and nitrogen could be detected by allowing the apparatus to return to room temperature after the test, it was assumed that this reaction did not occur. Also, a test using a solution of approximately 98 mole % hydrazine and 2 mole % water failed to indicate any thermal decomposition to ammonia and nitrogen for times corresponding to those of the duration of the runs. Thus the conclusion logically followed that any deviation of the measured pressure at a given temperature from the calculated perfect gas pressure was due to the dissociation of the hydrazine hydrate to hydrazine and water.

The partial pressure of the species in equilibrium was calculated in the following manner. Let

y = mole fraction of N_2H_4 in original sample
P = total pressure of gases at equilibrium
P^0 = total pressure of gases assuming complete dissociation
p_{HH} = equilibrium pressure of $N_2H_4 \cdot H_2O$
p_H = equilibrium pressure of N_2H_4
p_W = equilibrium pressure of H_2O

be the quantities relating to the equilibrium

$$N_2H_4 \cdot H_2O(g) = N_2H_4(g) + H_2O(g) \qquad (1)$$

The partial pressures for each of the components may be obtained directly in terms of P^0 and P.

$$p_{HH} = P^0 - P \qquad (2)$$

$$p_H = P - (1 - y)P^0 \qquad (3)$$

$$p_W = P - yP^0 \qquad (4)$$

At high temperatures where $p_{HH} \sim 0$, $P = P^0$, and the observable pressure P follows the perfect gas law $P = P^0 = nRT/V$. This curve can be extrapolated to low temperatures to give the P^0 values in the region of partial dissociation. A typical curve for P^0 and P *vs.* temperature is shown in Fig. 1.

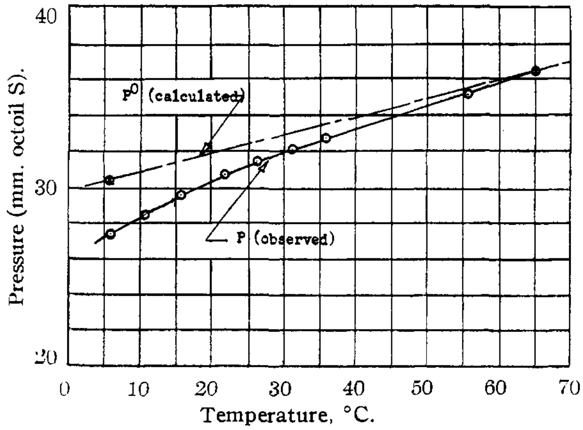

Fig. 1.—Calculated total gas pressure P^0 and observed pressure P *vs.* temperature for a typical system.

The equilibrium constants for the dissociation were calculated from the expression

$$K = p_H \, p_W / p_{HH} \qquad (5)$$

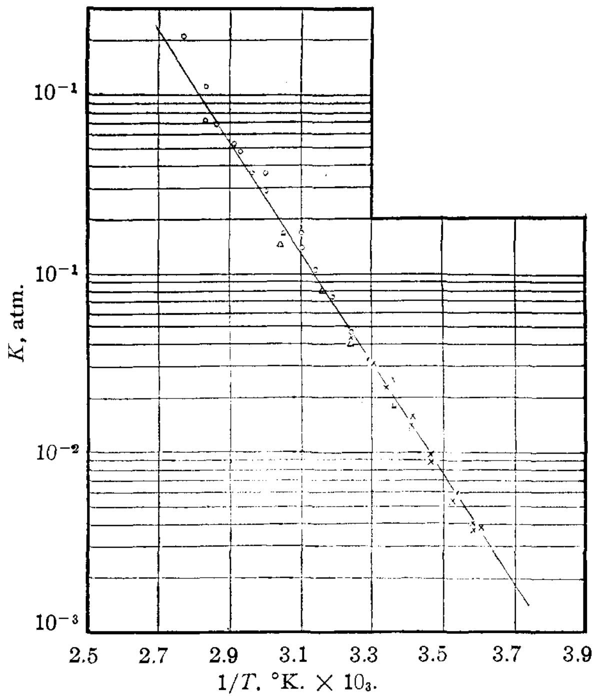

Fig. 2.—System: O, 53.6 mole % N_2H_4; X, 35.2 mole % N_2H_4; Δ, 21.55 mole % N_2H_4.

Figure 2 contains a graph of thirty-seven experimental values of K plotted against the reciprocal of the absolute temperature $1/T$. It will be observed that the values form a fairly straight line with no observable curvature in the temperature range covered These values may be represented by the following equation which was obtained by a least-squares calculation on the data

$$\log K_{atm} = -\frac{3054}{T} + 8.55 \qquad (6)$$

The value of K at 98.8° calculated from this equation is 2.19 atmospheres, whereas the value calculated at this Laboratory from A. Scott's data[4] on vapor density measurements was 0.244 atmosphere. Since his value is a single-point determination and in terms of the heat of reaction is irreconcilable with his measurement at 138°, it is believed to be in error.

IV. Thermodynamic Constants

The heat of the dissociation ΔH was calculated from the slope of the log K *vs.* $1/T$ curve, and the following value was obtained

$$\Delta H = 13.97 \pm 0.10 \text{ kcal.} \qquad (7)$$

Since no curvature is observed in this plot, and since the average temperature is only slightly above 298°K., this value may be taken as the standard ΔH°_{298}. Applying the Gibbs–Helmholz equation at 298°K., the entropy change for the reaction is obtained.

$$\Delta S^\circ_{298} = 39.1 \pm 0.4 \text{ cal./}^\circ \qquad (8)$$

Recently D. W. Scott, *et al.*,[7] have determined the standard entropy of $N_2H_4(g)$ and have calculated it to be 57.4 cal./°/mole. Combining this value with the standard entropy of $H_2O(g)$, which is 45.1 cal./°/mole, and with ΔS°_{298} given in Equation (8), the following value is obtained for the entropy of $N_2H_4 \cdot H_2O(g)$

$$S^\circ_{298}[N_2H_4 \cdot H_2O(g)] = 57.4 + 45.1 - 39.1 = 63.4 \text{ cal./}^\circ\text{/mole} \quad (9)$$

The heat of formation of hydrazine hydrate can be obtained from the heats of formation of $N_2H_4(g)$,[7] and from the heat of dissociation. The value obtained is

$$\Delta H_f^{298}[N_2H_4 \cdot H_2O(g)] = 22.75 - 57.80 - 13.97 = -49.02 \text{ kcal./mole} \quad (10)$$

V. Discussion

An analysis of the pressure–temperature relation of a hydrazine and water gas mixture shows that a hydration reaction occurs in which the hydrate is in equilibrium with its constituents. The facts that the slope of the pressure curve is a uniform and monotonic function of the temperature and that the log K is linear with the reciprocal temperature are offered as evidence for the existence of only one hydrate, the monohydrate, in the temperature and pressure range $5 < t < 90°$ and $2 < p < 10$ mm. This conclusion is in agreement with that drawn by Semishin[2] for hydrazine hydrate in the liquid phase as a result of his melting-point measurements.

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A New Boron Base, $Na_2HB(CH_3)_2$

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Upon contact with sodium in liquid ammonia at −78°, $(CH_3)_4B_2H_2$ is split equally into $(CH_3)_2BH \cdot NH_3$ (recognized by its later conversion to volatile $(CH_3)_2BNH_2 + H_2$) and the new salt $Na_2HB(CH_3)_2$. This reaction can be made quantitative because the ammoniation of $(CH_3)_4B_2H_2$, to form a solute which reacts with sodium in liquid ammonia to liberate one equivalent of H_2, is so much slower than the corresponding reaction of B_2H_6 that it does not compete. The salt $Na_2HB(CH_3)_2$ is stable as a white solid *in vacuo* even at 90°. It hydrolyzes rapidly and quantitatively to $(CH_3)_2BOH$, $2H_2$ and $2NaOH$. Dissolved in liquid ammonia, it is yellow, diamagnetic, well ionized, and unstable relative to disproportionation—a reaction promoted by $(CH_3)_4B_2H_2$. In liquid methyl ether it passes a filter but is highly aggregated—possibly colloidal. The $HB(CH_3)_2^{=}$ ion has high base-strength, expected because of a pair of unshared electrons on B, and demonstrated by the addition of $B(CH_3)_3$ in liquid ammonia to form a yellow solution of $Na_2HB(CH_3)_2 \cdot B(CH_3)_3$. This is stable *in vacuo* at 100° and probably is B–B bonded. Addition in the same ratio occurs also in liquid methyl ether, but the product loses the $B(CH_3)_3$ *in vacuo* at 25°. Here it is probable that $NaHB(CH_3)_3$ is formed (but easily converted to trimethylboron and sodium hydride), in view of other evidence that the reactions of $Na_2HB(CH_3)_2$ in methyl ether are hydridic—thus SiH_3Cl is converted to SiH_4. The fate of the $B(CH_3)_2^-$ residue of such reactions is uncertain.

Tetramethyldiborane[2] reacts with ammonia at −78°, presumably forming $NH_4(CH_3)_2BH(NH_2)BH(CH_3)_2$, but the process is far slower than the analogous reaction of diborane,[3–5] for the $(CH_3)_4B_2H_2$–NH_3 mixture must remain for at least 90 minutes at −78° before one can demonstrate, by introducing sodium and measuring the resulting hydrogen, the availability of one ammonium ion per mole. If very little time for ammoniation is allowed, as when tetramethyldiborane is brought immediately into contact with a melting solution of sodium in liquid ammonia, the solution turns green (or yellow if the sodium is not in excess) and no hydrogen is obtained even after many hours at −78°. The B-content of the tetramethyldiborane now can be recovered as equimolar proportions of two products, one of which decomposes at room temperature to form one mole each of hydrogen and the volatile $(CH_3)_2BNH_2$[6] (ammonolysis of a dimethylborine group) and the other of which is easily hydrolyzed to yield only hydrogen, $(CH_3)_2BOH$,[2] and NaOH in proportions indicating the formula $Na_2HB(CH_3)_2$.

The conditions for such a result are very specific. The sodium must be used in excess and the removal of the solvent ammonia (first by vacuum sublimation at −78° or lower) must be completed by successive treatments with pure trimethylamine until no more emerges at −50°. Then after the removal of hydrogen and $(CH_3)_2BNH_2$ *in vacuo* at room temperature, the non-volatile product is extracted from the excess sodium by liquid methyl ether at −40°. Attempts to simplify the process by using just two gram atoms of sodium per mole of tetramethyldiborane, or by omitting the use of trimethylamine to eliminate all but one mole of ammonia, lead to solid products containing more than half of the boron, part of which comes off as $B(CH_3)_3$ upon hydrolysis.

The Constitution of $Na_2HB(CH_3)_2$ in Terms of Its Chemical Behavior.—Cryoscopic and conductance measurements on the liquid ammonia solution of the product empirically designated as $Na_2HB(CH_3)_2$ clearly indicate the monomeric but fairly well ionized salt implied by the formula as written. However, in liquid methyl ether this salt is highly aggregated, for it does not appreciably lower the vapor tension of the solvent. In this possibly colloidal solution it behaves as a source of hydride, reacting mole-for-mole with SiH_3Cl to yield an amount of SiH_4 corresponding to all of the non-C–H hydrogen. The high availability of hydride from $Na_2HB(CH_3)_2$ (however it may be

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[1] Abstracted from a dissertation presented by George W. Campbell, Jr., to the Faculty of the Department of Chemistry, University of Southern California, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, February, 1951. Presented in substance at the XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., September, 1951.

[2] First prepared by H. I. Schlesinger and A. O. Walker, THIS JOURNAL, **57**, 621 (1935).

[3] A. Stock and E. Pohland, *Ber.*, **59B**, 2213 (1926).

[4] H. I. Schlesinger and A. B. Burg, THIS JOURNAL, **60**, 290 (1938).

[5] A. B. Burg, *ibid.*, **69**, 747 (1947).

[6] H. I. Schlesinger, L. Horvitz and A. B. Burg, *ibid.*, **58**, 409 (1936).