atm. make it probable that an effect as great as that shown in the table would not occur. It was finally decided to use the equation given by Keyes[14]

$$V_t^{Fe} = V_0(1 + 3.25 \times 10^{-5}t + 2.85 \times 10^{-8}t^2 - 1.65 \times 10^{-11}t^3)$$

where V_0 is the volume at 0° and V_t the volume at temperature t. This formula gives linear coefficients for the ranges 0–200 and 0–300° which are about the averages of the two sets given in Table I. The possible error in the determination of volume incurred at 0 and 50° is probably not more than one or two parts in 10,000, since the absolute values were known at 25 and 100°. At 200 and 300° the error introduced in V_t^{Fe} using the above equation is estimated between 0.05–0.10%. This does not influence the relative precision of any one isotherm. A change in the value of the reference point will affect all the other values by the same fractional amount.

Our experimental data are shown in Table II, and also data from Bartlett, Michels, and Holborn and Otto, where we have no values of our own. Since the data of Michels for nitrogen were given at odd pressures, we have used his equations to calculate the values given in this table. Dr. Deming expects to calculate the thermodynamic properties of hydrogen–nitrogen mixtures from these data.

We want to thank Dr. E. J. Jones for assistance in setting up our thyratron temperature control and Lola S. Deming (Mrs. W. E. D.) for helping us in our calculations. We also acknowledge the help of Mr. J. R. Dilley, who assisted in the design of the high pressure equipment.

Summary

Previous work since 1930 on the compressibilities of hydrogen, nitrogen and their mixtures has been summarized. A modified Bartlett compressibility apparatus is described. The compressibilities of hydrogen and four hydrogen–nitrogen mixtures have been measured at 0, 25, 50, 100, 200 and 300° and to 1000 atmospheres.

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[14] Keyes, Joubert and Smith, *J. Math. Phys. Mass. Inst. Tech.*, 1, 191 (1922).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF MERCK AND CO., INC.]

The Hydration of Vitamin B_1

BY W. A. BASTEDO, JR., N. R. TRENNER AND T. J. WEBB

Introduction

The marked deliquescence of vitamin B_1[1] has been recognized by many investigators. The water of crystallization, however, has been given variously in the literature as one-half, one, or approximately one molecule of water (per molecule of vitamin) without regard for the conditions of humidity. The problem of preparing the one or more supposed hydrates in pure form and the measurement of their dissociation pressures was undertaken in these Laboratories. In the beginning the problem proved to be baffling on account of lack of reproducibility. This initial lack of reproducibility in the degree of hydration was attributed finally to variable minor details in the later stages of preparation of the vitamin, such, for example, as solvents used in the precipitation process, methods of removing solvent, etc. After standard procedures having regard for such details had been found, the early difficulties regarding reproducibility disappeared (at least to the extent of 0.1 g. of water per 100 g. of vitamin). The much higher reproducibility obtainable for samples under identical conditions of humidity led to the belief that the remaining difficulty lay in the inherent problem of the reproducibility of the aqueous pressures to which the samples were exposed. The fact that *slight* variations in the aqueous pressures to which the samples were exposed gave rise to appreciably variable water contents of the vitamin indicated immediately that the problem was not one of an ordinary system of hydrates.

Experimental Details and Results

In the first attack on the problem the aqueous pressure to which the samples were exposed was regulated by H_2SO_4–H_2O mixtures in evacuated desiccators at 25 ± 1°.

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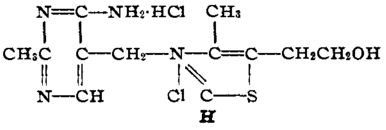
[1] Formula of vitamin B_1



Ninety-five per cent. sulfuric acid was found to be a complete desiccant for the vitamin. The density of the mixtures was measured with sufficient accuracy that the aqueous pressure could be found to within approximately 0.4 mm. of mercury by reference to standard measurements.[2,3] In order to check this procedure for obtaining a given aqueous pressure saturated solutions of calcium chloride and of barium chloride were used on two occasions. The results obtained with these solutions were entirely consistent with those obtained with the H_2SO_4–H_2O mixtures. Two days were sufficient for the samples (approximately 0.6 g.) to attain equilibrium with a given aqueous pressure. Weights (accurate to 0.1 mg.) were always checked on the third day, and in many cases after the lapse of one or more weeks. The water contents of the vitamin in terms of grams of water per 100 g. of anhydrous vitamin are given in Table I for various aqueous pressures (expressed in mm. of mercury). Each entry represents an average of a number of determinations—in the range of aqueous pressures above 7 mm., some of the entries represent an average of as many as ten determinations. The variations were of the order of 0.1 g. of water per 100 g. of vitamin. The large number of determinations represents an attempt to distinguish between a number of hydrates of very nearly the same water content.

TABLE I

Aqueous press.	Water, %	Aqueous press.	Water, %
1.2	0.46	6.8	4.31
1.4	.70	9.0	4.52
2.0	1.62	10.0	4.60
3.0	2.07	10.8	4.62
3.3	2.59	12.2	4.72
3.6	2.88	14.6	4.93
5.0	3.62	15.3	4.91
5.9	4.12	18.2	5.15

A graph of the results in Table I shows that within the estimated experimental error they can be represented by a smooth curve (Fig. 1) and give no evidence whatever of definite stoichiometric hydrates except in the extent to which there is an approach to one molecule of water per molecule of vitamin at high aqueous pressures. The region of experimental values was terminated naturally by the aqueous pressure of the saturated solution, 20.9 mm. A slight extrapolation of the experimental curve indicates that approximately one molecule of water per molecule of vitamin (in the crystalline state) would be acquired at 20.9 mm. The curve is reproducible in a hydrating as well as a dehydrating sense. The complete reversibility of the hydration and dehydration phenomena, which is often not observed in the case of continuous hydration,[4] precludes the possibility that the hydration is a slow process not attaining equilibrium. On the other hand, the absence of definite stoichiometric hydrates would seem to indicate that the forces exerted by the water molecule in the crystal play little, if any, role in the crystal lattice. The shape of the curve exhibiting the water content as a function of the aqueous pressure is strongly suggestive of a sorption process only in the range of high aqueous pressures. It is possible that the hydration phenomena observed in this case are not uncommon in the case of deliquescent organic substances of complicated structure—the assignment of definite formulas for such hydrates often being merely a matter of rounding out the results of chemical analysis.

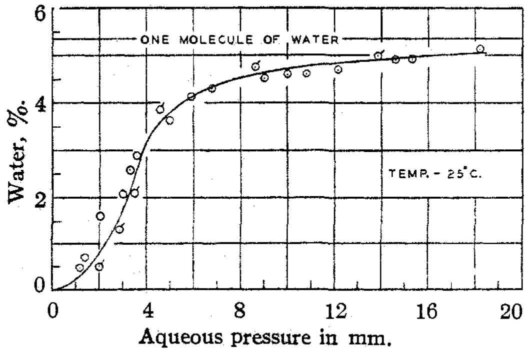


Fig. 1.—Hydration of vitamin B_1: results of gravimetric method, ⊙; volumetric method, ⊙-.

The fact that the type of result obtained above was entirely unexpected and practically without mention in standard works on the subject of salt–hydrates led to a renewed attack with an entirely different technique. A thoroughly dried sample of the vitamin was placed in an all-vacuum apparatus of the type described by Taylor and Strother[5] for sorption problems. A constant aqueous pressure was automatically preserved in the system and the decrease in the volume of water vapor measured to 0.01 cc., the temperature of the sample of vitamin being held accurately at 25°. Corrections were applied for the dead space in the vessel containing the sample and for the adsorption on the walls of the container. The latter effect could be represented accurately by an equation of the form

$$x = kp^n$$

x being the quantity adsorbed and p the aqueous pressure. The constants k and n were found to have the values 0.0184 and 0.68, respectively,

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[2] "International Critical Tables," Vol. III, 1938, p. 56.

[3] Collins, *J. Phys. Chem.*, **37**, 1191 (1933).

[4] *Cf.* the case of Zeolites, "Inorganic Chemistry," by Ephraim, English edition, 1934, p. 756.

[5] Taylor and Strother, THIS JOURNAL, **56**, 586 (1934).

if x is expressed in cc. (N. T. P.) and p in millimeters of mercury. The results obtained in this way checked those obtained by the first method, within the experimental error (estimated to be at least as great as two parts of water per 1000 of vitamin). The error in this method is as large as this in view of the fact that the samples of vitamin were necessarily very small—of the order of 2 mg. The discrepancy between the two sets of experimental results corresponds to an error of 0.004 mg. in the weighings. By this method the percentages of water in the vitamin under aqueous pressures of 14.0, 9.0, 4.57, 3.0 mm. were found to be 5.00, 4.80, 3.85, and 1.3, respectively. The results are exhibited graphically in Fig. 1. These results were considered an adequate check of the results by the first method, and it therefore seemed unnecessary to question further the continuity of this hydration phenomenon.

The second series of measurements reveals the actual speed of the hydration process as carried out (Fig. 2). It is to be noted that the time required for virtual completion of the hydration process (*e. g.*, curve C) was strictly comparable with that required for the virtual completion of the adsorption process on the glass (curve D) *i. e.*, of the order of two hours. The readings corresponding to the points representing the times labeled ∞ were taken after approximately twenty-four hours and indicate that equilibrium had been reached.

The vapor pressure of the saturated solution of vitamin B_1 was measured in the usual type of differential tensimeter, a mineral oil of specific gravity 0.894 being used as the manometric liquid. Water was used as a balancing liquid in one limb of the tensimeter and the saturated solution of the vitamin in the other. The results for several temperatures are given in Table II in terms of mm. of mercury.

TABLE II

VAPOR PRESSURE OF SATURATED SOLUTION

Temp., °C.	25	24	23	20	15	106
Press., mm.	20.9	19.6	18.5	15.4	11.4	8.0

A straight line is obtained when the logarithm of the vapor pressures is plotted against the reciprocal of the absolute temperature. The slope of this line indicates that the heat of vaporization of one mole of water from the saturated solution is 10,800 cal. (*cf.* 10,450 cal. for the molal heat of vaporization of pure water at 25°).

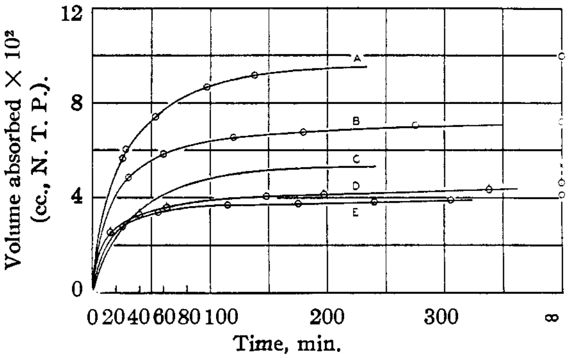

Fig. 2.—Rate of absorption of water on 2.019 mg. of vitamin B_1 at 25°: Curve A, absorption on vitamin + glass at 3.57 mm.; Curve B, absorption on vitamin + glass at 2.90 mm.; Curve C, Curve A − Curve D; Curve D, absorption on glass walls at 3.57 mm.; Curve E, absorption on vitamin + glass at 2.05 mm.

Summary

The degree of hydration of vitamin B_1 at 25° was determined gravimetrically at sixteen different aqueous pressures in the range between 1 and 19 mm. The degree of hydration was found to increase continuously from approximately 0.4% of water at 1 mm. to 5.20% at 19 mm. At the aqueous pressure of the saturated solution (20.9 mm.) the degree of hydration of solid vitamin corresponds approximately to one molecule of water of crystallization per molecule of vitamin. These determinations were checked by a volumetric method in which the volume of water vapor absorbed by the vitamin at various pressures of water vapor was measured. The vapor pressure of the saturated solution of the vitamin was measured over a temperature range in the neighborhood of room temperature.

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