solubility or penetration occurs.   If only one individual is hydrated no generalization can as yet be made.

Summary

1. The conversion of hydroxyvaleric acid into valerolactone under the catalytic influence of hydrogen ion is shown to be a bimolecular process, the reaction actually measured being the rate of effective collision between the suitably activated hydroxyvaleric acid and the hydrogen ion.

2. A characteristic bimolecular constant is obtained at a given temperature, which is not altered by change in concentration of the catalyst, or by the presence of sucrose, potassium chloride, or lithium chloride in the reaction mixture.   This constant involves the activities of the reactants, and also the viscosity of the solution raised to a power characteristic of the hydrogen ion.   This power is not a constant, but varies with the relative size of the individuals in the solution, as determined independently from electrical-conductivity measurements.

3. There is a sharp contrast in behavior between the water of hydration of sucrose, on the one hand, and that of potassium and lithium chlorides on the other, in respect of the effect upon the hydroxyvaleric acid molecule. The water of hydration of sucrose is not available as solvent, whereas that of the neutral salts is available.   In none of these cases, however, is hydrogen ion soluble in water of hydration.   The point is considered, but no definite conclusion is arrived at.

4. The true critical increment of the reaction is found to be 12,750 calories per mole of hydroxyvaleric acid transformed.   This value is considerably less than the corresponding value obtained on the assumption that the reaction is unimolecular, the difference being 3,000 calories per mole.   The unimolecular critical increment has, however, no real significance for the process actually measured, which is shown to be truly bimolecular.

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STUDIES ON CERTAIN PHYSICAL PROPERTIES OF ARSENIC TRIOXIDE IN WATER SOLUTION

BY ERNEST ANDERSON AND LEROY G. STORY

Notwithstanding the enormous amount of investigational work on arsenic trioxide, some important physical properties of this substance are not accurately known.   For this reason it seemed desirable to make determinations of the density, refractive index, solubility and hydrogen-ion concentration of aqueous solutions of this substance as well as of the amount of arsenious acid formed in such a solution.

Purification of the Arsenic Trioxide

Arsenic trioxide was purified by recrystallization from hydrochloric acid as follows. Forty g. of the oxide was dissolved in 50 cc. of hot conc. acid, the solution diluted with 50 cc. of water, filtered immediately from any residue and 50 cc. more of water added to the filtrate.[1] The solution was cooled, and the crystals were filtered off and washed with ice water until free from chlorides. This procedure yields the octahedral form which was used in the investigation.

The Density and Refractive Index of Aqueous Solutions

The determination of the density of aqueous solutions was made at 25° by weighing a pycnometer full of water and afterwards full of the aqueous solution of arsenic trioxide. The densities given are, therefore, referred to water at 25° as unity. When the density referred to water at 4° is desired it is necessary to multiply the densities given in Table I by the density of water at 25°, that is 0.997077.

The determination of the refractive index was made at 22° by a sensitive immersion refractometer. The data found are recorded in Table I, both in refractive indices and in scale readings.

All of the curves for the density, refractive index and scale reading plotted from the data in Table I are straight lines to which the equation $W = A + Bx$ applies, where W is the weight of material in grams per liter, A and B are constants and x is the density at 25°, the refractive index or immersion scale reading at 22°. The values of the constants A and B determined as an average from Table I give Equation 1 where densities are used, Equation 2 where refractive indices are used and Equation 3 where scale readings are used. (1) $W = -1288.36 + 1288.39x$; (2) $W = -10062.7 + 7550x$; (3) $W = -42.95 + 3.04x$.

TABLE I

DENSITY AND REFRACTIVE INDEX OF AQUEOUS SOLUTIONS OF ARSENIC TRIOXIDE

As$_2$O$_3$ per liter of solution G.	Density at 25°		Refractive index at 22°		Immersion scale reading 22°	
	Found	Calc.	Found	Calc.	Found	Calc.
1.796	1.0014	1.0014	1.33309	1.33305	14.71	14.71
3.212	1.0025	1.0025	1.33326	1.33324	15.15	15.17
3.580	1.0029	1.0029	.....	1.33328	...	15.30
5.060	1.0039	1.0039	1.33348	1.33348	15.75	15.78
5.670	1.0044	1.0044	1.33355	1.33355	15.90	15.98
6.425	1.0050	1.0050	1.33363	1.33366	16.23	16.23
7.184	1.0057	1.0056	1.33376	1.33376	16.45	16.48
7.4366	....	1.0058	1.33381	1.33380	16.60	16.57
8.561	1.0068	1.0068	1.33393	1.33394	16.89	16.93
10.13	1.0080	1.0080	1.33417	1.33415	17.53	17.46
11.35	1.0089	1.0089	1.33432	1.33431	17.93	17.86
12.85	1.0102	1.0100	1.33450	1.33452	18.38	18.35
14.368	1.0113	1.0112	1.33469	1.33471	18.88	18.85

[1] The statement of Wood, *J. Chem. Soc.*, **93**, 413 (1908), that As$_2$O$_3$ is least soluble in approximately 3.2 N hydrochloric acid was checked and found correct.

A brief examination was made of the influence of temperature on the refractive index. The results showed that from approximately 21° to 27° each increase of 1° caused a decrease of 0.25 on the immersion refractometer scale or a decrease of 0.000097 in the refractive index.

Solubility in Water

Numerous investigators have studied the solubility of arsenic trioxide in water[2] but the results have been conflicting. Probably this is due in part to the fact that equilibrium is reached very slowly and in part to the use of different forms of the substance.
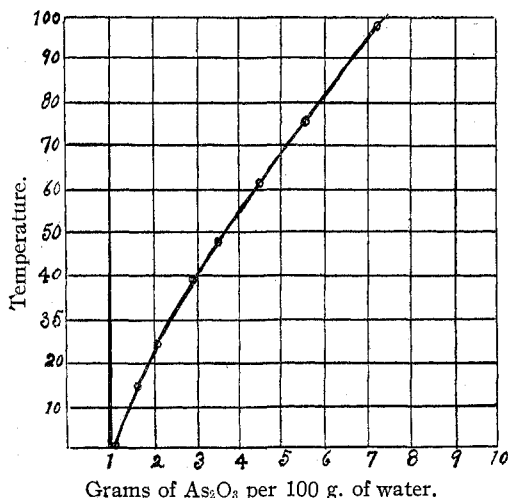

Fig. 1.—Solubility curve for arsenic trioxide in water.

Grams of As_2O_3 per 100 g. of water.

In this investigation, bottles containing water and excess of arsenic trioxide were shaken mechanically in a bath of boiling water until analysis showed that equilibrium had been reached. This required approximately 2 days. The solubility at lower temperatures was determined by placing the hot saturated solution in a thermostat at the desired temperature and shaking it until analysis showed that equilibrium had been reached. At 25° this required approximately 10 days while at 0° it required 2 weeks. As a check on some of these determinations, the solubility was also determined by mixing the trioxide and water, warming to the desired temperature and stirring until equilibrium was reached.

TABLE II

SOLUBILITY OF ARSENIC TRIOXIDE IN WATER

Temperature °C.	As₂O₃ per 100 g. of H₂O		Temperature °C.	As₂O₃ per 100 g. of H₂O	
	Found G.	Calc. G.		Found G.	Calc. G.
0	1.21	1.21	48.2	3.43	3.40
15	1.66	1.64	62	4.45	4.45
25	2.05	2.05	75	5.62	5.63
39.8	2.93	2.85	98.5	8.18	8.18

The dissolved trioxide was determined by weighing approximately 15 cc. of the solution, diluting and titrating the trioxide with standard iodine

² Clayton, *Chem. News*, **64**, 27 (1891). Chadounsky, *Chem. Centr.*, **1889**, 569. Winkler, *J. prakt. Chem.*, **31**, 247 (1885). Brunner and Talloczko, *Z. anorg. Chem.*, **37**, 456 (1903).

solution in the presence of sodium bicarbonate. The data obtained are recorded in Table II. The solubility curve plotted from these data is given in Fig. 1. It was found possible to represent this curve by the equation, $W = A + Bt + Ct^2$, where W is the weight of solute in g. per 100 g. of water, t is the temperature and A, B and C are constants whose values are, respectively, 1.21, 0.021 and 0.000505.

The Hydrogen-ion Concentration of a Water Solution of Arsenic Trioxide at 25°

Numerous attempts were made to determine the hydrogen-ion concentration of a water solution of arsenic trioxide by means of the hydrogen electrode but the results were unsatisfactory, probably because of reduction of the substance.[3] The colorimetric method for determining hydrogen-ion concentrations[4] was finally used on a saturated solution in water. This gave a Sörensen value of 6.6 at 25° when either phenol red or bromothymol blue was used.

The Conversion of Arsenic Trioxide into Arsenious Acid

Zawidski found that the molecular weight of arsenic trioxide in water solution[5] was 101.5. The present investigation gave the molecular weight 92.5 by the boiling-point method and 99.17 by the freezing-point method. Apparently at 0° the trioxide is converted completely into some form of arsenious acid, possibly $HAsO_2$. Work is being continued on the application of the phase rule to the system, calcium oxide-arsenic trioxide-water and to other arsenites.

Summary

Accurate data are given for the density, refractive index, solubility, hydrogen-ion concentration and molecular weight of arsenic trioxide in water solution.

LINCOLN, NEBRASKA

[3] Gladstone and Tribe, *J. Chem. Soc.*, **33**, 306 (1878). William Thompson, *Chem. News*, **99**, 157 (1909).

[4] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., **1920.**

[5] Zawidski, *Bull. soc. chem.*, **30**, 1162 (1903); *Ber.*, **36**, 1427 (1903).