the average values obtained for both alpha and beta glucose are given as follows, expressed in common logarithms with the time expressed in minutes:

Temp. °C.	25	35	45
$(k_1 + k_2) \times 10^4$	1.8 ± 0.4	3.4 ± 0.3	9.0 ± 0.5

Worley and Andrews[2] noted a divergence from a first-order reaction for about twenty minutes for both alpha- and beta-*d*-glucose in water at 0°. Since the velocity of mutarotation in absolute methanol is 0.00018 at 25° compared to 0.00073 for water at 0°, the divergence should extend over a period of about one hundred and fifty minutes. During the present investigation, in no case was a lag noticed during the first two hours of mutarotation of the alpha sugar in absolute methanol and no acceleration during a like period in the case of the beta sugar.

Though the velocity constants $(k_1 + k_2)$ are the lowest and most consistent so far reported in the literature, they are not constant enough to calculate an exact value for the energy of activation for the mutarotation of *d*-glucose in methanol. However, using the average values for $(k_1 + k_2)$ at 25, 35 and 45°, a mean value of 15,000 cal./mole is obtained from the Arrhenius equation. If the lowest values obtained at 25° (0.00014) and 45° (0.00085) are used, an activation energy of 17,000 cal./mole is obtained. This value agrees with that obtained for the mutarotation in water solution[9] and appears to justify the assumption that the mechanism of mutarotation is the same in methanol as in water.

The initial rotations for both alpha- and beta-*d*-glucose were obtained graphically by extrapolating the first-order equation to zero time. The initial specific rotation of alpha-*d*-glucose in absolute methanol was found to be $[\alpha]_D$ +115.5 ± 0.5°, compared to +111.0° for the same sugar in water solution. The corresponding value for the beta-*d*-glucose was $[\alpha]_D$ +17.0 ± 0.5°, compared to +19.5° for a water solution. These values were the same for all three temperatures investigated within experimental error.

The specific rotation for the equilibrium mixture of alpha- and beta-*d*-glucose was found to be $[\alpha]_D$ +66.5 ± 0.3° in absolute methanol compared to +52.6° in water. If it is assumed that only two forms of sugar are present, the equilibrium mixture of *d*-glucose in methanol contains 50.1% of the alpha form and 49.9% of the beta form. In water solution the equilibrium mixture contains 36.4% alpha and 63.6% beta-*d*-glucose. These results are in qualitative agreement with other workers[2,7] who found that the percentage of alpha-*d*-glucose in the equilibrium mixture was increased in absolute methanol. However, Worley and Andrews[2] report 44.3% alpha- and 55.7% beta-*d*-glucose in the equilibrium mixture. To check the composition of the equilibrium mixture, samples were made up from the pure alpha and beta sugars in proportions reported by Worley and Andrews and also in the proportions found in this investigation. The sample with the composition reported here gave the equilibrium rotation immediately and showed no change of rotatory power on standing. The sample with the composition reported by Worley and Andrews gave an initial reading of +58.4° and on standing slowly changed, giving a final equilibrium rotation of +66.3°.

The results of this study do not exclude the possibility of forms other than the alpha- and beta-*d*-glucose being present in solution. However, if there are other forms present, their concentration must be too small to be detected by this method. A recent communication by Cantor and Peniston[10] indicates that the amount of the aldehyde isomer in an aqueous solution of *d*-glucose is considerably less than 0.3%.

(9) G. F. and M. C. Smith, *J. Chem. Soc.*, 1413 (1937).

(10) Cantor and Peniston, This Journal, **62**, 2113 (1940).

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The Mutarotation of alpha-*d*-Glucose in Ethanol–Water Mixtures at 25°[1]

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The mutarotation of alpha-*d*-glucose in water solutions has been investigated many times under various conditions, but the studies of this phenomenon in non-aqueous solutions are not so numerous. Recent work in this Laboratory[2] using pure methanol as a solvent confirmed the previously observed fact that physical quantities associated with this phenomenon are markedly different in various solvents. Since marked changes were noticed in absolute methanol, it was decided to investigate the mutarotation in ethanol. Due to the slight solubility of alpha-*d*-glucose in

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(1) Presented before the Division of Physical and Inorganic Chemistry at the Cincinnati meeting, April, 1940.

(2) Rowley and Bailey, This Journal, **62**, 2562 (1940).

absolute ethanol, it was found necessary to determine these physical properties in mixtures of ethanol–water. Previous work along this line has been reported by Levy,[3] Trey[4] and Hudson and Yanovsky[5] at 20°. The present work was done at 25° and in mixtures ranging up to 93.7% ethanol by weight for values of the velocity constants ($k_1 + k_2$) and up to 98.7% for the equilibrium rotation. By graphical extrapolation it was possible to determine reasonable values for the initial specific rotation, the equilibrium specific rotation and the reaction rate for absolute ethanol.

Discussion of Results

The solutions were made by dissolving a weighed amount of pure anhydrous alpha-*d*-glucose in ethanol–water mixtures of known composition. The mutarotation was followed polarimetrically in jacketed tubes using a sodium arc as a light source. The concentrations ranged from 2.5 g. of sugar/100 ml. of solution for the low alcohol concentrations to 0.6 g. of sugar/100 ml. of solution for the high ethanol concentrations.

A summary of the values for the initial specific rotation, the equilibrium specific rotation and the velocity constants ($k_1 + k_2$), expressed in common logarithms with the time expressed in minutes, is given in Table I. These values were read directly from large graphs of the original data.

As has been found by many previous workers, the rate of mutarotation of alpha-*d*-glucose follows a first-order reaction which can be expressed by an equation[6] involving the initial rotation, the equilibrium rotation and the rotation at a specific time. The deviation from a first-order reaction found by Worley and Andrews[7] was not found during this investigation. This confirms the findings of Isbell and Pigman[8] and agrees with the results obtained in this Laboratory with absolute methanol solutions.[2]

It is seen from the table that the addition of small amounts of ethanol to water has a much greater effect in reducing the rate of mutarotation than the addition of water to ethanol has in increasing the rate. This is in agreement with the results of Worley and Andrews[7] working with methanol–water mixtures. The extrapolated value for the velocity of mutarotation in absolute ethanol at 25° is less than in methanol (0.00018), as was found qualitatively by Trey.[4]

As the alcohol concentration increases, the value of the equilibrium specific rotation also increases gradually to about 80% ethanol by weight. However, above 80% ethanol the rise becomes much more rapid, giving an extrapolated value of +65.5° for absolute ethanol. Trey[4] reported a specific equilibrium rotation of +62.4° in absolute ethanol. The value reported here is slightly lower than the value of +66.5° obtained in absolute methanol but, allowing for the experimental difficulties, this is not considered significant. Andrews and Worley[7] obtained an almost linear relationship for the change of the specific rotation at equilibrium in methanol–water mixtures. However, their points are scattered and only one value is given for concentrations of methanol above 60% by weight.

The initial specific rotation values were obtained in most cases by extrapolating the first-order equation to zero time. Above ethanol concentrations of 90%, this method could not be used due to experimental difficulties. However, by utilizing the equation for determining the half-life period of a first-order reaction, it is possible to calculate the value of the initial specific rotation in the higher concentrations if the equilibrium rotation is known. As in the case of the equilibrium specific rotation, the specific initial rotation is lowered considerably by the addition of water to ethanol but is raised only slightly by the addition of ethanol to water. The value obtained for absolute ethanol appears to be a trifle higher than the value of +115.5° obtained for absolute methanol.

TABLE I

SUMMARY OF RESULTS

Wt. % C_2H_5OH	Init. rotn. $[\alpha]^{2}_{D}$	Equil. rotn. $[\alpha]^{25}_{D}$	$(k_1 + k_2) \times 10^3$
0	110.5	52.6	10.5
10	110.5	53.1	7.7
20	110.6	53.6	6.3
40	110.8	54.8	4.4
60	111.0	56.3	3.1
80	111.6	58.6	1.7
90	112.6	60.7	0.95
95	114.2	62.6	0.55
100	116.2	65.5	0.10

Attention should be called to the fact that the values given in the "International Critical Tables"[9] for the initial specific rotation and

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[3] Levy, *Z. physik. Chem.*, **17**, 317 (1895).

[4] Trey, *ibid.*, **18**, 193 (1895).

[5] Hudson and Yanovsky, THIS JOURNAL, **39**, 1013 (1917).

[6] Hudson, *ibid.*, **26**, 1065 (1904).

[7] Worley and Andrews, *J. Phys. Chem.*, **31**, 742, 1880 (1927); **32**, 307 (1928).

[8] Isbell and Pigman, *J. Research Natl. Bur. Standards*, **18**, 141 (1937).

[9] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., Vol. II, 1928, p. 347–348.

equilibrium specific rotation of *d*-glucose in absolute ethanol are in error. The data given in the "Tables" are taken from the work of Hudson and Yanovsky[5] and apply to absolute methanol, not absolute ethanol.

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Note on the Arrangement of Phases in Palladium-Hydrogen

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The existent studies of palladium by methods of X-ray diffraction, now more than a dozen in number,[2] show the system to include two phases, both of face centered cubic type, but of widely differing lattice constants, and having compositions which vary over considerable ranges. Since these investigations have been carried out under conditions not suited to make clear the spatial arrangement of the phases, it seemed desirable to show that, as is to be expected in a diffusion system, the two phases of this typical hydrogen alloy are completely segregated, and that changes in gross composition are accompanied by migration of the phase boundary.

The palladium used was about 99.85% pure and had the form of a ribbon of 5 × 0.05 mm. cross section. This ribbon was suspended vertically in a tube 2 cm. in diameter, consisting of thin celluloid cemented to glass end-pieces, which was borne by an adjustable support provided with a vertical scale. A back reflection camera was employed, with a slit system such that the irradiated area on the specimen extended one millimeter vertically by four millimeters across the strip horizontally. The target was of iron, and the distance between specimen and film was 6 cm. The containing tube was filled to 3.2 cm. above the bottom of the ribbon with 2 N sulfuric acid, and during the series of observations the palladium was continuously charged by passing into the immersed portion a current of 5 milliamperes from an adjacent anode of platinum foil. The palladium at the level of the electrolyte had therefore a fixed hydrogen concentration corresponding to a cathodic current density of approximately 0.16 amp./sq. dm.

Preliminary exposures, made after some hours of electrolysis, gave the diffraction spectrum of the β phase only, from a region in the palladium one millimeter above the electrolyte level; while at a point several millimeters higher, the spectrum of the α phase was alone observed. It was also found that whereas exposures of three-quarters of an hour were required to yield a visible β phase pattern on an unrotated film, diffraction from the α phase was sufficiently intense to give a clear result in ten minutes. For following the progress of the diffusion, exposures of ten or fifteen minutes were therefore made, and the absence of any pattern was taken as showing the presence of the β phase in the region observed. The results are displayed in Table I, where time is taken from the beginning of measurements, after the full saturation of the metal below the electrolyte, and distance is measured upward from the level of the liquid.

TABLE I

Film	Time, hr.	Distance, mm.	Phase	Rate of boundary migration
12	4.5	4	α	$\eqslantgtr$ 1 mm. in 5 hr.,
13	5.0	1	β	or 0.20 mm./hr.
14	5.7	3	α	
15	22.5	3	β	$\eqslantless$ 4 mm. in 23.3 hr.,
16	23.3	5	α	or 0.17 mm./hr.
18	24.3	4	α	
20	46.5	4	β	$\eqslantless$ 6 mm. in 47.6 hr.,
21	47.6	6	α	or 0.126 mm./hr.
22	50.7	7	α	

As may be seen from this table, the boundary steadily advanced from the line at which the hydrogen concentration was kept constant, the rate declining from a value exceeding 0.20 mm. per hour to a value less than 0.126.

The method employed could doubtless be made to serve for exact observation of the rate of diffusion, unaffected by factors introduced by the entry and exit of hydrogen at the metal surfaces. Since this, however, would involve a determination of the relation between the cathodic current density and the hydrogen concentration attained in the cathode, and since the diffusion constant obtained would be valid for the metal only in the precise physical condition in which it was examined, we have here contented ourselves with demonstration of the qualitative relationships.

The results show clearly the division of the alloy into two distinct phases, one of which (α) occupies all of the region in which the concentration of hydrogen is below a certain saturation

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[1] Associate Professor of Chemistry, Princeton University.

[2] Most recent studies E. A. Owen and J. Idwal Jones, *Proc. Phys. Soc. London*, **49**, 587, 603 (1937); A. Michel, *Bull. assoc. tech. fonderie*, **12**, 302 (1938).