their power of dissolving metals. Lithium is found to be soluble in ethylamine and potassium in ethylenediamine. In the higher members of the primary amines as well as in the secondary and tertiary amines, the alkali metals are insoluble. The behavior of mixed solvents has also been studied. As a rule, the alkali metals are soluble in any inactive solvent containing considerable ammonia, and the solubility is the lower the smaller the amount of ammonia present. If sufficient metal be added to a solvent containing ammonia, the system, in general, separates into two liquid phases which differ markedly in their content of metal as well as in appearance. A similar separation takes place when salt is added to a metal solution in ammonia.

Dilute solutions of the compound $NaPb_2$ are shown to be electrolytic in nature. An investigation of the products of electrolysis of these solutions indicates that the ions Na^+ and Pb_2^- are present, since two gram-atoms of lead are transferred from the cathode to the anode for one equivalent of electricity. A number of reactions in which this compound takes part have been studied and the results are in accord with this hypothesis. Tin likewise is soluble in an ammonia solution of sodium.

The form of the solubility curve for sodium in ammonia is in part given, in part conjectured from indirect observations. It is shown that over a limited range of concentration two solutions of sodium coexist. Both contain less than 15 per cent. of sodium (according to the formula weight), and their critical point of solution lies in the neighborhood of —50° and 10 per cent. of sodium.

A study is made of the rate of the reaction, $Na + NH_3 = NaNH_2 + \frac{1}{2}H_2$ as it takes place in a sealed tube at different times. After an initial period of some days, during which the rate of reaction is nearly constant, a great acceleration is observed. This acceleration is probably due to the catalytic action of solid sodamide, which begins to precipitate out after a time. Contrary to the observations of Joannis, there is no indication that the rate of the above reaction is retarded by the presence of hydrogen gas.

Boston, September 7, 1907.

THE CATALYSIS BY ACIDS AND BASES OF THE MUTAROTATION OF GLUCOSE.

By C. S. Hudson.

The mutarotation[1] of aqueous solutions of glucose follows the formula of a monomolecular reaction. As is well known its rate is enormously

[1] This term which has been introduced by T. M. Lowry is here adopted in preference to the words "birotation" and "multirotation," as a name for the slow change in the power of rotating polarized light that is shown by freshly prepared solutions of glucose and other related sugars.

influenced by the temperature of the solution and by the presence in it of acids and bases, but on the other hand no strong accelerative action is exerted by neutral substances which do not undergo hydrolysis in solution.   Acids and bases are also specific catalyzers of the mutarotation of milk-sugar, while neutral substances are in this case also without comparable influence.   This fact that only the hydrogen and hydroxyl ions are strong catalyzers of the mutarotation of these two sugars deserves careful study because such a peculiar specific catalytic action is probably intimately related with the causes of the mutarotation.   The present article presents measurements that were undertaken in order to determine what relation exists between the concentration of the catalyzing agent and the amount of its accelerative action.   These measurements show that the relationship over the whole range of acid and alkaline solutions and pure water can be expressed by a simple formula which can also be derived theoretically from simple assumptions.

Measurement of the Rate of Mutarotation in Acid Solutions Near 25°.

The following experiments were made with a polariscope sensitive to 1/20 degree using a jacketed observation tube 20 cm. long which was kept at a constant temperature of 24.°7 by a stream of water supplied from a large thermostat.   The solutions were prepared by dissolving four grams of anhydrous crystalline d-glucose, of the best quality that is supplied by Kahlbaum, in twenty cubic centimeters of distilled water or hydrochloric acid solutions of different strengths, filtering, and observing the angle of rotation at intervals during about one hour.   The first measurements were taken ten minutes or in some cases five, after the glucose was mixed with the water, and the final constant rotation was obtained by adding two or three drops of strong ammonia to the solution in the polariscope tube.   For all the concentrations of acid that were used duplicate experiments were made and the agreement was uniformly good ; the following table contains the results of all the experiments that were performed.   The time is expressed in minutes, the reading of the polariscope in degrees, and the velocity-constant of the reaction, k, is calculated from the usual formula, $k = \frac{1}{t} \log \cdot \frac{r_0 - r_\infty}{r - r_\infty}$, using common logarithms.

It is apparent from the data given in the following table that the rate and the acid concentration bear a linear relation to each other and that a minimum rate occurs in weakly acid solutions. Although this minimum rate is difficult to detect with certainty, its presence can hardly be doubted because two other observers, Trey[1] and Lowry[2], have also found that the rate is

[1] Trey, Z. physik. Chem., **22,** 443, 448 (1897). See also Osaka, Z. physik. Chem., **35,** 702 (1900).

[2] Lowry, J. Chem. Soc., **83,** 1314 (1903).

TABLE I

RATE OF MUTAROTATION OF GLUCOSE IN HYDROCHLORIC ACID SOLUTIONS AT 24.°7.

No.	Concentration HCl (mol./liter)	Reading at time									k
		0	5	15	25	35	45	60	∞		
1	Distilled	34.2	32.4	29.2	27.0	25.3	24.0	22.5	18.5	0.0106 }	0.0106
2	Water	32.8	30.8	28.4	25.8	24.2	22.8	21.5	17.7	0.0107 }	
3	0.001	33.9	32.2	29.3	26.7	25.1	23.7	22.2	18.0	0.0099 }	0.0098
4	0.001	32.7	30.8	28.2	26.2	24.4	22.8	21.2	17.2	0.0098 }	
5	0.005	32.5	30.6	27.8	25.3	23.6	22.2	20.8	17.5	0.0112 }	0.0112
6	0.005	32.6	30.7	27.6	25.4	23.6	22.0	20.7	17.4	0.0113 }	
7	0.01	32.4	30.4	27.4	24.8	23.1	21.5	20.2	17.3	0.0120 }	0.0121
8	0.01	33.2	31.2	28.0	25.5	23.6	22.2	20.8	18.0	0.0122 }	
	time	0	5	15	20	25	30	∞			
9	0.03	32.4	29.7	27.3	25.4	23.8	22.7	21.8	16.7	0.0168 }	0.0169
10	0.03	31.8	29.3	26.8	24.9	23.5	22.3	21.3	16.6	0.0170 }	
11	0.06	33.7	29.8	26.8	24.7	22.8	21.5	20.7	17.7	0.0244 }	0.0253
12	0.06	34.7	30.6	27.3	25.2	23.7	22.3	21.5	18.8	0.0262 }	
13	0.10	32.3	27.4	23.8	21.7	20.3	19.3	...	17.4	0.0357 }	0.0354
14	0.10	31.4	27.0	23.7	21.9	20.4	19.6	...	17.8	0.0352 }	

slightly less in weakly acid solutions than in pure water. This depression will be further considered later on.

A Formula for the Rate of Mutarotation in Acidic and Basic Solutions.

Osaka[1] has concluded from his measurements on the rate of mutarotation in acid and basic solutions that the rate is proportional to the concentration of hydroxyl ions in the basic solutions, but proportional to the square root of the concentration of the hydrogen ions in the acid solutions. While these conclusions express Osaka's measurements very well, it will be seen later in this article that they do not agree with those measurements of mine in acid solutions, which refer to concentrations outside the limits, 0.02 to 0.06 molal, studied by Osaka. And particularly they do not agree with the fact that a minimum rate occurs in weakly acid solutions. It is therefore necessary to seek some other expression for the rate in acid and alkaline solutions, one which shall take account especially of the depression of the rate in weakly acid solutions.

The simplest assumption regarding the influence of acids and bases on the rate of mutarotation is that both the hydrogen and hydroxyl ions accelerate the reaction and that the increase in the rate is proportional to the increase in concentration of the two kinds of ions. We should thus have $\Delta k = B\Delta(H^{\cdot}) + C\Delta(OH')$ and therefore $k = A + B(H^{\cdot}) + C(OH')$, where k is the rate of mutarotation in a solution which contains hydrogen and hydroxyl ions in the concentrations $(H^{\cdot})$ and (OH') respectively, and A, B, and C are constants. To obtain the values of these the preceding data on acid solutions have been used in connection with Osaka's measurements in basic solutions. Osaka's value for the rate in pure water is 0.0104, which agrees closely with the value that I have found, 0.0106, showing that the two sets of measurements were made at the same temperature, although slightly different values for it were

[1] Loc. cit.

found, namely 25° and 24.°7. Using the rates of the preceding table (I), A is found to have the value 0.0096 and B, 0.258, and the measurements of Osaka on basic solutions shown in the following table (II) give 9750 as the value of C. The formula for the rate of mutarotation of glucose at 25° in pure water or in acid or basic solutions is, therefore,

$$k = 0.0096 + 0.258(H^{\cdot}) + 9750(OH').$$

In the following table are given the rates that Osaka has observed in basic solutions and those which I have found in acid solutions with the corresponding rate that is calculated from the above formula[1]. It will be seen that the formula expresses the rate over the complete range of concentration with an accuracy that is well within the errors of observation.

TABLE 2

COMPARISON OF OBSERVED AND CALCULATED RATES.

No.		Molal Con-centration	Rate		Diff.	Observer
			Observed	Calculated		
1		0.0000022 (OH')	0.0326	0.0310	+.0016	Osaka
2		0.0000033	0.0382	0.0418	—.0036	"
3	Alkaline	0.0000031	0.0446	0.0398	+.0048	"
4		0.0000044	0.0494	0.0486	+.0008	"
5		0.0000055	0.0640	0.0632	+.0008	"
6		0.0000066	0.0705	0.0739	—.0034	"
7	Pure Water	0.00000012	0.0106	0.0108	—.0002	Hudson
8		0.001 (H')	0.0098	0.0099	—.0001	"
9		0.005	0.0112	0.0109	+.0003	"
10	Acid	0.01	0.0121	0.0122	—.0001	"
11		0.03	0.0169	0.0173	—.0004	"
12		0.06	0.0253	0.0250	+.0003	"
13		0.10	0.0354	0.0354	.0000	"

This table shows that there is a distinct depression of the rate in weakly acid solutions, its value for pure water being 0.0106 but for 0.001 HCl only 0.0098. The cause of this depression is obviously that the addition of small quantities of acid to pure water lowers the concentration of hydroxyl ions to nearly as great an extent as the increase in hydrogen ions and as the former are far stronger catalytic agents than the latter, the rate of mutarotation is necessarily decreased. But after the hydroxyl ions have been considerably reduced, further addition of acid accelerates the rate because the hydroxyl ions are now in such very small concentration that their further reduction is no longer of influence upon the rate. There must thus be a minimum rate in acid solutions; the concentration of acid which gives this minimum rate can be readily calculated from the formula above. Writing the first differential of k with respect to $(H^{\cdot})$ equal to zero and solving gives $(H^{\cdot}) = 2.3(10)^{-5}$ mols/liter. In an

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[1] In calculating the rate in solutions from the above formula it is to be remembered that the product of the concentration of the hydrogen and hydroxyl ions is the dissociation-constant of water, $1.4(10)^{-14}$ at 25°. The equation can therefore be expressed in the form $k = 0.0096 + 0.258(H^{\cdot}) + \dfrac{(9750)(1.4)(10)^{-14}}{(H^{\cdot})}$, in which k and $(H^{\cdot})$ are the only variables.

acid solution of this strength the rate is therefore minimum and has the value 0.0096, which is ten per cent. less than the rate for pure water. The concentration of acid which gives the same rate as pure water can likewise be found from the formula by writing $k = 0.0106$ and solving the resulting quadratic equation for $(H\cdot)$, which gives the value 0.004 mols/liter. We can therefore conclude that *acid solutions containing hydrogen ions in less strength than 0.004 molal retard the mutarotation of glucose, and those of greater strength accelerate it*. This conclusion from the above measurements is further supported by the previously mentioned observations of Trey and Lowry. Trey found that the rate was slightly depressed in one-tenth normal solutions of acetic and propionic acids, its value being 0.0082 in these solutions and 0.0087 in pure water. These acids are approximately one per cent. dissociated in tenth normal solution and the hydrogen ion concentration in them is therefore 0.001, which is within the region where a depressed rate of mutarotation is to be expected from the formula. Lowry observed a slight decrease of the rate in 0.001 and 0.0001 molal hydrochloric acid solutions, which are also within the region of depressed rates.

In conclusion the following table is given in support of the assumption that has been made in deriving the preceding formula, that the increase of the rate in acid solutions of appreciable strength is proportional to the increase in the concentration of the hydrogen ions. It will be seen from it that the numbers given in the fourth column agree as well as could be expected in such measurements, but on the other hand, the proportion factor given in the third column varies in a regular manner, showing that the rate is not proportional to the square root of the hydrogen ion concentration.

TABLE 3
RELATION BETWEEN THE ACID CONCENTRATION AND THE RATE.

Acid Concentration $(H\cdot)$	Rate k	$\dfrac{k}{\sqrt{(H\cdot)}}$	$\dfrac{\Delta k}{\Delta(H\cdot)}$	Observer
0.001	0.0098	0.310	....	Hudson
0.0245	0.0172	0.110	0.315	Osaka
0.0323	0.0186	0.102	0.281	"
0.0480	0.0244	0.112	0.311	"
0.0633	0.0277	0.110	0.289	"
0.005	0.0112	0.158	0.280	Hudson
0.01	0.0121	0.121	0.230	"
0.03	0.0169	0.098	0.237	"
0.06	0.0253	0.103	0.258	"
0.10	0.0354	0.112	0.256	"

Summary.

1. Measurements of the rate of mutarotation of glucose at 24.°7 in acid (HCl) solutions between the strengths 0.001 and 0.1 molal have been made. They show that there is a linear relation between the hy-

drogen ion concentration and the rate of mutarotation in solutions of such acid strength that the influence of the hydroxyl ions upon the rate can be neglected.

2. The conclusion of Osaka that the rate of mutarotation is proportional to the square root of the hydrogen ion concentration holds fairly well between the concentrations 0.01 to 0.10 molal but does not agree at all well with measurements outside this region of concentration.

3. Using Osaka's values for the rate in alkaline solution and new values for it in acid solutions, it is found that the following formula expresses accurately the rate of mutarotation of glucose at 25° in pure water and in acid and alkaline solutions.   Rate = 0.0096 + 0.258($H^{\cdot}$) + 9750(OH').

4. Hydroxyl ions are nearly forty thousand times stronger catalyzing agents of the mutarotation of glucose than hydrogen ions.

5. This stronger catalyzing action of the hydroxyl ions causes a lower rate of mutarotation in weakly acid solutions than is observed for pure water. This depression of the rate, or "negative catalysis", has been measured in a 0.001 molal hydrochloric acid solution and found to be in close agreement with the predictions of the above formula.

The measurements recorded in this article were made possible by the kindness of Professor Geo. A. Hulett, who allowed the author the use of of his well equipped laboratory at Princeton University.

Newport News, Virginia.

COLLODION MEMBRANES.

By S. Lawrence Bigelow and Adelaide Gemberling.

Contents.

Bibliographical.—Comparison of dialysis through collodion, parchment paper and gold beater's skin.—The quantity of water which passes through collodion at a definite temperature and pressure.—Pressure and temperature coefficients.—The effect of thickness on the permeability.—The permeabilities of different samples of collodion.—The effect of age on the permeability. Summary.

The convenience and usefulness of collodion membranes are not, at the present time, fully appreciated by chemists and physicists.   This article contains a brief bibliography, methods for making these membranes and an account of our experiments.

Bibliographical.

The first mention of collodion membranes as applied to diffusion phenomena, which we have found, is in an article by A. Fick[1].   He recognized their advantages but had difficulties in fastening them onto holders

[1] Ueber Diffusion. Pogg. Annal., **94**, 59-86 (1855).