

mined by the thermodynamic stability of the various isomers.

Summary

1. The results of tritium exchange between hydrogen, hydrogen chloride, and butanes during isomerization are presented. These show that exchange of tritium in hydrogen chloride to butane

is large compared to exchange of tritium in hydrogen (HT) to butane.

2. A mechanism is proposed which qualitatively explains the data.

3. A general mechanism of hydrocarbon isomerization is presented.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The First Ionization of Carbonic Acid in Aqueous Solutions of Sodium Chloride

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From the electromotive forces of the cells without liquid junction

Pt-H₂, CO₂|NaHCO₃(*m*₁), NaCl(*m*₂), CO₂(*m*₃)|AgCl-Ag
Harned and Davis² determined the first ionization constant of carbonic acid in water. They also showed that this cell may be used to determine the ionization, $m_{\text{H}}m_{\text{HCO}_3}/m_{\text{CO}_2}$, in salt solutions if the solubility of carbonic dioxide in these solutions is known and, as a contribution to this objective, they measured m_{CO_2} in sodium chloride solutions at concentrations up to 3 *M* and throughout the temperature range 0 to 50°.

We have now extended these cell measurements in a manner suitable for the determination of the ionization in sodium chloride solutions up to a concentration of 1 *M* salt and at temperatures from 0 to 50°. From these ionization data, the heat content, specific heat and entropy of ionization have been computed over the above ranges of concentration and temperature.

A very careful analysis of the equilibrium data has been made and equations constructed by which the ionization constant, $K_{(S=0)}$, the ionization, $K_{(S)}$, the molalities, m_{H} and m_{CO_2} , and the activity coefficients, $\gamma_{\text{H}}\gamma_{\text{HCO}_3}/\gamma_{\text{CO}_2}$, may be calculated with a high order of accuracy.

General Method of Procedure

The equation for the electromotive force, *E*, of the cell is

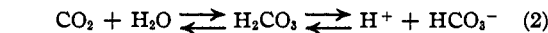
$$\begin{aligned} E &= E^0 - \frac{RT}{F} \ln m_{\text{H}}m_{\text{Cl}}\gamma_{\text{H}}\gamma_{\text{Cl}} + \frac{RT}{2F} \ln P_{\text{H}_2} \\ &= E^0 - E_c - \frac{RT}{F} \ln m_{\text{H}}m_{\text{Cl}}\gamma_{\text{H}}\gamma_{\text{Cl}} \end{aligned} \quad (1)$$

where E^0 is the standard potential at one atmosphere hydrogen pressure, E_c equals $(-RT/2F) \ln P_{\text{H}_2}$ and the other symbols have their usual significance.³ The dissociation equilibrium under consideration is given by

(1) This communication contains material from a dissertation presented by Francis T. Bonner to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1944.

(2) Harned and Davis, *THIS JOURNAL*, **65**, 2030 (1943).

(3) For a thorough discussion of this method as applied to other equilibria involving hydrogen ion, see Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," chapter 15, Reinhold Publishing Corporation, New York, N. Y., 1943.



and the ionization constant is defined by

$$K_{(S=0)} \equiv \frac{a_{\text{H}}a_{\text{HCO}_3}}{a_{\text{CO}_2}a_{\text{H}_2\text{O}}} = \frac{\gamma_{\text{H}}\gamma_{\text{HCO}_3}m_{\text{H}}m_{\text{HCO}_3}}{\gamma_{\text{CO}_2}a_{\text{H}_2\text{O}}m_{\text{CO}_2}} = \frac{\gamma_{\text{H}}\gamma_{\text{HCO}_3}}{\gamma_{\text{CO}_2}a_{\text{H}_2\text{O}}} K_{(S)} \quad (3)$$

As a reference state, we choose the condition that $\gamma_{\text{H}} = \gamma_{\text{HCO}_3} = \gamma_{\text{CO}_2} = a_{\text{H}_2\text{O}} = 1$ in pure water at every temperature, and therefore $K_{(S=0)}$ becomes an isothermal constant at all salt concentrations.

By elimination of m_{H} from equations (1) and (3), the expression used by Harned and Davis for the determination of $K_{(S=0)}$

$$\begin{aligned} -\log K' &= -[\log K_{(S=0)}] + \log \frac{\gamma_{\text{H}}\gamma_{\text{Cl}}a_{\text{H}_2\text{O}}\gamma_{\text{CO}_2}}{\gamma_{\text{H}}\gamma_{\text{HCO}_3}} = \\ &(E + E_c - E^0) \frac{F}{2.303RT} + \log m_{\text{CO}_2} + \log \frac{m_{\text{Cl}}}{m_{\text{HCO}_3}} \end{aligned} \quad (4)$$

is obtained. Since the logarithmic term containing the activity coefficients becomes unity in pure water, $[-\log K_{(S=0)}]$ may be obtained by extrapolating the right side of this equation to zero concentrations of all solutes. This requires a double extrapolation, firstly to zero concentration of electrolytes and finally to zero concentration of carbon dioxide. Harned and Davis, by employing gas mixtures containing from 18 to 80% carbon dioxide showed that the presence of carbon dioxide had no appreciable effect upon $[-\log K']$. This important fact eliminates the necessity of the double extrapolation and greatly reduces the number of measurements required.

By elimination of $\log K_{(S=0)}$ from equations (3) and (4), we obtain

$$\begin{aligned} -\log \frac{m_{\text{H}}m_{\text{HCO}_3}}{m_{\text{CO}_2}} &= (E - E^0 + E_c) \frac{F}{2.303RT} + \\ &\log \frac{m_{\text{CO}_2}m_{\text{Cl}}}{m_{\text{HCO}_3}} + \log \gamma_{\text{H}}\gamma_{\text{Cl}} \end{aligned} \quad (5)$$

an expression which may be used to evaluate the ionization, $m_{\text{H}}m_{\text{HCO}_3}/m_{\text{CO}_2}$, henceforth denoted by $K_{(S)}$, in the salt solutions. We note that this evaluation of $K_{(S)}$ does not require a knowledge of $K_{(S=0)}$. If the activity coefficient function, $\gamma_{\text{H}}\gamma_{\text{HCO}_3}/\gamma_{\text{CO}_2}a_{\text{H}_2\text{O}}$, is required, it is apparent from equation (3) that a knowledge of $K_{(S=0)}$ is necessary.

To evaluate $[-\log K_{(S)}]$ at a given sodium

TABLE I

OBSERVED ELECTROMOTIVE FORCES OF THE CELLS; Pt-H₂, CO₂|NaHCO₃(*m*₁), NaCl(*m*₂), CO₂(*m*₃)|AgCl-Ag

*P*_B, barometric pressure in mm., is given in parentheses immediately following *E*_i. Gas composition is given in % by volume. Last column contains (-log *m*₃) corresponding to the temperature designated. Series (1): %H₂ = 44.09; %CO₂ = 55.91; *m*₂ = 0.1.

Cell number.....1	2	3	4	5	6	(-log <i>m</i> ₃) (<i>m</i> ₂ = 0)
<i>m</i> ₁0.005035	0.007478	0.01000	0.01497	0.01999	0.02994
<i>E</i> ₂₅ (756.0) .61228	.62245	.62988	.64019	.64781	.65762	1.7440
<i>E</i> ₃₀ (754.0) .61756	.62768	.63543	.64591	.65332	.66374	1.8056
<i>E</i> ₃₅ (753.1) .62282	.63312	.64100	.65166	.65922	.66980	1.8636
<i>E</i> ₄₀ (753.2) .62826	.63875	.64673	.65759	.66523	.67604	1.9185
<i>E</i> ₄₅ (753.0) .63379	.64434	.65254	.66334	.67142	.68236	1.9726
<i>E</i> ₅₀ (753.3) .63928	.65015	.65830	.66940	.67753	.68860	2.0255
<i>E</i> ₂₅ (751.8) .61238	.62234	.62994	.64015	.64765	.65781	1.7466
<i>E</i> ₂₅ (755.8) .61217	.62245	.62978	.64019	.64768	.65772	1.7441
<i>E</i> ₀ (759.3) .58629	.59632	.60240	.61205	.61915	.62808	1.3816
<i>E</i> ₅ (757.8) .59130	.60043	.60770	.61733	.62390	.63343	1.4637
<i>E</i> ₁₀ (758.0) .59639	.60564	.61313	.62288	.62958	.63924	1.5402
<i>E</i> ₁₅ (756.2) .60168	.61107	.61869	.62862	.63546	.64541	1.6129
<i>E</i> ₂₀ (757.4) .60664	.61663	.62413	.63425	.64135	.65140	1.6795
<i>E</i> ₂₅ (759.3) .61222	.62244	.62983	.64021	.64768	.65771	1.7421

chloride molality according to equation (5), a series of cells may be measured at a constant value of *m*_{Cl} and a number of varying dilute concentrations of sodium bicarbonate. With these data an extrapolation of the right side of this equation to zero bicarbonate molality may be made since *E* is the measured electromotive force, *E*_c may be calculated from the hydrogen pressure, *E*⁰ is known, *m*_{CO₂}, *m*_{Cl} and *m*_{HCO₃} are known from the solution composition and $\gamma_{H}\gamma_{Cl}$ is the square of the activity coefficient of hydrochloric acid at zero concentration in sodium chloride at a concentration, *m*_{Cl}. The carbon dioxide molality may be obtained from the partial pressure of this substance in the gas mixture and the Henry's law constants given by Harned and Davis by the equation

$$m_{CO_2} = S_{(g)}P_{CO_2} \quad (6)$$

This extrapolation yields [-log *K*_(s)] at zero bicarbonate solution and at an *m*_{CO₂} in the salt solution corresponding to *P*_{CO₂}. If $\gamma_{H}\gamma_{Cl}$ were known in the solution containing both bicarbonate and sodium chloride, then [-log *K*_(s)] could be evaluated exactly in these solutions. In absence of this knowledge, $\gamma_{H}\gamma_{Cl}$ in sodium chloride at a molality equal to the sum of the chloride and bicarbonate molalities should be a good approximation for practical computations. This matter will receive careful consideration in a separate section.

Experimental

The experiments were performed in cells similar to those described by Harned and Davis.² The only modification consisted in placing the hydrogen and silver chloride electrodes in the two compartments rather than in the same compartment. The tube joining these two chambers was fitted with a stopcock which was closed at all times except when an actual measurement was in progress. This prevented the diffusion of silver chloride, which dissolves more readily in the concentrated salt solutions, from entering the hydrogen electrode vessel. Deposition of silver upon

the hydrogen electrode occurs when this precaution is overlooked.

The concentrations of the electrolyte constituents of the cells were determined to within $\pm 0.05\%$. The composition of the gas mixture entering the cell, determined by an Orsat apparatus, was evaluated to within $\pm 0.1\%$. Five complete series of results were obtained at constant salt concentrations of 0.1, 0.2, 0.5, 0.7 and 1 *M*. At each fixed salt concentration, the six sodium bicarbonate concentrations constituting a series of cells were approximately 0.0005, 0.0007, 0.01, 0.015, 0.02 and 0.03 *M*. In order to cover the entire temperature range from 0 to 50°, it was necessary to make two series of measurements. One series covering half the range required thirty-six to forty-eight hours. Under the conditions of these experiments, the silver chloride electrodes have been found to deteriorate after two days. The high temperature series was started at 25°, then the temperature increased in five degree intervals to 50°, following which a recovery measurement was made at 25°. The low temperature measurements were made at 25°, then 0° and at 5° intervals to 25°. The agreement of the readings at the beginning and end of the series was employed as a criterion of successful operation. In nearly all cases the differences in electromotive forces at the beginning and end of run were considerably less than 0.2 mv.

Since the results are so voluminous we have included in Table I the observations at only one of the sodium chloride concentrations, or one-fifth the actual number of measurements. This table also includes the barometric pressures, the gas composition and the solution composition which in addition to the values of *E* constitute all the data necessary for the calculations.

Details of Calculation of the Ionization, *K*_(s).—From the barometric pressure, the composition of the gas entering the cell and the vapor pressure of water over the sodium chloride solutions, the partial pressures *P*_{H₂}, *P*_{CO₂} and *P*_{H₂O} in the cell were calculated. The vapor pressures of the salt solutions were obtained from the "International Critical Tables."⁴ Linear interpolation of these data was required. *E*_c was then evaluated and *m*_{CO₂} computed by equation (6) using values of *S* read from plots of (-log *S*) versus salt concentration at each temperature.

(4) "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., 1929, Vol. III, p. 370.

TABLE II

SMOOTHED VALUES OF $[-\log K_{(s)}]$. NUMBERS IN PARENTHESES ARE THE FOURTH DECIMAL PLACE DEVIATIONS
(OBSERVED - SMOOTHED VALUES)

$m_{\text{NaCl}} \dots 0$	0.1	0.2	0.5	0.7	1.0	
0	6.5773	6.3486 (24)	6.2882 (25)	6.2055 (-8)	6.1789 (24)	6.1537 (-15)
5	6.5171	6.2873 (-7)	6.2272 (-25)	6.1465 (-14)	6.1217 (-37)	6.0981 (-15)
10	6.4647	6.2336 (-17)	6.1740 (-14)	6.0949 (+20)	6.0721 (0)	6.0499 (17)
15	6.4200	6.1876 (-12)	6.1283 (-22)	6.0508 (-3)	6.0296 (-5)	6.0087 (-6)
20	6.3823	6.1484 (-13)	6.0894 (18)	6.0134 (-23)	5.9936 (5)	5.9736 (-34)
25	6.3514	6.1157 (34)	6.0567 (26)	5.9824 (14)	5.9635 (13)	5.9443 (29)
30	6.3270	6.0892 (-5)	6.0301 (-6)	5.9575 (3)	5.9391 (-11)	5.9201 (5)
35	6.3086	6.0683 (-7)	6.0091 (-12)	5.9380 (20)	5.9197 (-12)	5.9004 (9)
40	6.2960	6.0529 (14)	5.9935 (21)	5.9236 (23)	5.9050 (33)	5.8850 (-4)
45	6.2891	6.0340 (10)	5.9835 (12)	5.9140 (-13)	5.8946 (-18)	5.8739 (16)
50	6.2873	6.0379 (-6)	5.9786 (-5)	5.9094 (-13)	5.8885 (-11)	5.8671 (-3)

The data of Harned and Davis² were employed in constructing these plots. The values of E^0 used were those of Harned and Ehlers.⁵

Since m_1 and m_2 are known, the only other quantity required is the activity coefficient product, $\gamma_{\text{H}^+}\gamma_{\text{Cl}^-}$, at zero concentration in the salt solution of the ionic strength of the cell. Values of this quantity in 0.01 *M* hydrochloric acid in sodium chloride solutions are given by Harned and Owen.⁶ These were extrapolated to zero molality of hydrochloric acid and their logarithms plotted against the ionic strength at each temperature. The values substituted in equation (5) were read from these graphs at the ionic strengths of the cells.

The characteristics of the extrapolations are clearly illustrated by Fig. 1 in which the right side of equation (5), computed from the data in Table I, is plotted against the bicarbonate

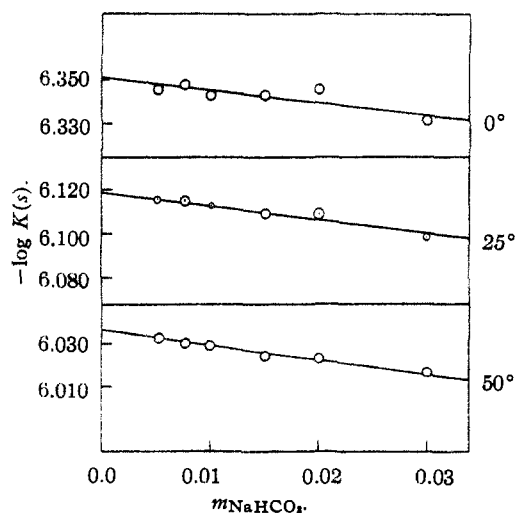


Fig. 1.—Extrapolations at 0, 25 and 50° at 0.1 *M* sodium chloride.

(5) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, N. Y., 1943, p. 330.

(6) Harned and Owen, *ibid.*, p. 375; the extrapolations to zero acid concentration were made by employing the constants α_n [Table (14.6.1)] in equation on p. 459.

molality. The radii of the circles for the 0 and 50° series are 0.1 mv. At 25°, the points represent the mean values of four results all of which lie within the limits indicated by the size of the circles. These plots are typical of all the extrapolations, none of which are less consistent than the 0° plot and few more consistent than the one at 50°. All the graphs are linear.

The values of $[-\log K_{(s)}]$ were then plotted against the temperature and from this graph the smoothed results given in Table II were obtained. The consistency of the data is shown by the deviations in parentheses. The average and maximum deviations were found to be 0.0015 and 0.0034, respectively. The results at zero salt concentration are those observed by Harned and Davis.

Calculation of Ionization Constant as a Function of Temperature and Derived Thermodynamic Quantities, ΔH_i^0 , ΔS_i^0 and $\Delta C_{p,i}^0$.—We have computed the ionization, $K_{(s)}$, as a function of temperature by the equation of Harned and Robinson⁷

$$\log K_{(s)} = -(A^*/T) + D^* - C^*T \quad (7)$$

The parameters of this equation, evaluated by the method of least squares, are compiled in Table III. With these constants, the results in Table II may be computed with a maximum deviation of 0.0011 and an average deviation of 0.0004.

TABLE III

m	A^*	D^*	C^*	T_θ	$-\log K_{(s)}$
0.0	3404.71	14.8435	0.032786	322.2	6.2885
.1	3266.11	14.0256	.030811	325.6	6.0376
.2	3228.50	13.8363	.030401	325.9	5.9780
.5	3158.38	13.5235	.029892	325.0	5.9075
.7	2955.23	12.2139	.027721	326.5	5.8885
1.0	2786.18	-11.1187	.025885	328.1	5.8661

The free energy, heat content, heat capacity and entropy of ionization may be calculated by the relations

$$\Delta F_i^0 = A' - D'T + C'T^2 \quad (8)$$

$$\Delta H_i^0 = A' - C'T \quad (9)$$

(7) Harned and Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940); see also Harned and Owen, *ref. 5*, pp. 512-514, 583-584.

$$\Delta C_{p1} = -2C'T \quad (10)$$

$$\Delta S_1^0 = D' - 2C'T \quad (11)$$

in which the primed constants equal the starred constants of equation (7) multiplied by 2.3026*R*. The temperature, T_θ , at which the ionization is a maximum and the value of $\log K_{(s)}$ at this temperature are given by

$$T_\theta = \sqrt{A^*/C^*} \quad (12)$$

$$\log K_{\theta(s)} = D^* - 2\sqrt{C^*A^*} \quad (13)$$

These latter quantities are listed in the last two columns of the table.

A Simplified Method for Computing the Ionization from 0 to 1 *M* and 0 to 50°.—By taking the negative of the logarithm of equation (3) and rearranging terms, we obtain

$$[-\log K_{(s)}] = [-\log K_{(s=0)}] + \log \gamma_H \gamma_{HCO_3} - \log \gamma_{CO_2} \alpha_{H_2O} \quad (14)$$

at a given temperature. Upon substituting the Debye and Hückel formula with an additional linear term for $\log \gamma_H \gamma_{HCO_3}$, this becomes

$$[-\log K_{(s)}] = [-\log K_{(s=0)}] - \frac{2S_{(t)} \sqrt{d_0} \sqrt{\mu}}{1 + A' \sqrt{\mu}} + B'\mu - \log \gamma_{CO_2} \alpha_{H_2O} \quad (15)$$

where $S_{(t)}$ and A' have their usual significance, μ is the ionic strength, and d_0 is the density of water. The activity coefficient of the carbon dioxide in the salt solution relative to its value in pure water is given by

$$\gamma_{CO_2} = S_{(s=0)}/S_{(s)} \quad (16)$$

where $S_{(s=0)}$ and $S_{(s)}$ are the Henry's law constants in water and salt solutions, respectively. Values of $\log \gamma_{CO_2}$, computed from the data of Harned and Davis² are a linear function of the salt molality.

$$\log \gamma_{CO_2} = \alpha\mu \quad (17)$$

over the concentrate in range 0 to 1 *M*. Further, the variation of $\log \alpha_{H_2O}$ from linearity will cause no appreciable difficulty. At 25°, this quantity computed from the osmotic coefficient may be expressed roughly to within 0.0002 by the equation

$$-\log \alpha_{H_2O} = \beta m = 0.0147 m \quad (18)$$

from 0 to 1 *M* sodium chloride. These considerations show that equation (15) may be reduced to the Debye and Hückel term plus a linear term. Finally we let A' equal unity at all temperatures. Equation (15) then reduces to the simplified form

$$[-\log K_{(s)}] = [-\log K_{(s=0)}] - \frac{2S_{(t)} \sqrt{d_0} \sqrt{\mu}}{1 + \sqrt{\mu}} + B\mu \quad (19)$$

where $[-\log K_{(s=0)}]$, $S_{(t)} \sqrt{d_0}$ and B are functions of the temperature. For this system, $[-\log K_{(s=0)}]$ is given by

$$-\log K_{(s=0)} = -3404.71/T + 14.8435 - 0.032786T \quad (20)$$

according to equation (7), and B may be computed satisfactorily by

$$B = 0.066 + 1.92 \times 10^{-3} t - 0.0176 \times 10^{-3} t^2 \quad (21)$$

where t is the centigrade temperature. Values of $S_{(t)} \sqrt{d_0}$ computed from the recent tables of Birge⁸ are given by the equation

$$S_{(t)} \sqrt{d_0} = 0.4883 + 0.75545 \times 10^{-3} t + 0.1743 \times 10^{-5} t^2 + 0.11665 \times 10^{-7} t^3 \quad (22)$$

obtained by Scatchard.⁹

The maximum deviation of the results computed by these equations from those in Table II is 0.0063 and occurs at 50° and 1 *M* salt. From 0 to 25° the maximum deviation is 0.0033. The average deviation increases gradually as the temperature rises being about 0.001 up to 10°, from 0.001 to 0.002 between 10 and 30°, and from 0.002 to 0.004 at the higher temperatures.

Since this trend parallels the experimental uncertainty, we have made no attempt to complicate this calculation by arithmetical refinements. The largest cause of uncertainty resides in the determination of the solubility of carbon dioxide. This error increases with temperature and at 50° may be as high as 1.5%. Although it is impossible to evaluate the over-all uncertainty exactly, a gross error estimation is useful. We shall assume an error in E of 0.1 mv. and 0.1% in the concentration of gas mixture, bicarbonate and sodium chloride molalities at all temperatures. At 0°, we shall assume that the uncertainty in carbon dioxide molality is 0.3% while at 50°, it is 1.5%. Further, the error in $\log \gamma_H \gamma_{Cl}$ necessary for the computation [Equation (5)] will be taken to be 0.001 at all temperatures. The added errors from all the sources lead to a gross error of 0.005 in $\log K_{(s)}$ at 0° and 0.01 at 50°. The above calculation lies well within these limits.

Further Detailed Discussions of the Equilibrium.—The above procedure leads directly to the evaluation of $K_{(s)}$ or $m_H m_{HCO_3}/m_{CO_2}$ and its computation by means of equation (19). Further, according to equations (3) and (19), the activity coefficient function is given by

$$\log \frac{\gamma_H \gamma_{HCO_3}}{\gamma_{CO_2} \alpha_{H_2O}} = \log K_{(s=0)} - \log K_{(s)} = -\frac{2S_{(t)} \sqrt{d_0} \sqrt{\mu}}{1 + \sqrt{\mu}} + B\mu \quad (23)$$

Since the Henry's constants are known these quantities can be subdivided further. From equations (16) and (17) we observe that

$$\log \gamma_{CO_2} = \log S_{(s=0)} - \log S_{(s)} = \alpha\mu \quad (24)$$

and from equation (6)

$$\log m_{CO_2} = \log S_{(s)} + \log P_{CO_2} \quad (25)$$

whence

$$\log m_{CO_2} = \log S_{(s=0)} P_{CO_2} - \alpha\mu \quad (26)$$

(8) Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

(9) Scatchard, *THIS JOURNAL*, **65**, 1249 (1943).

From the data of Harned and Davis

$$[-\log S_{(s=0)}] = -\frac{2385.73}{T} + 14.0184 - 0.015264T \quad (27)$$

and

$$\alpha = 0.1190 - 0.833 \times 10^{-3}t + 0.666 \times 10^{-5}t^2 \quad (28)$$

whence γ_{CO_2} and m_{CO_2} may be evaluated by equations (24) and (26) from 0 to 50° and from 0 to 1 *M* salt. Further, from equation (21) it follows that the ionic activity coefficient product may be expressed by

$$\log \gamma_{\text{H}}\gamma_{\text{HCO}_3} = -\frac{2S(t)\sqrt{d_0}\sqrt{\mu}}{1+\sqrt{\mu}} + B\mu + \log_{\text{CO}_2}\alpha_{\text{H}_2\text{O}} \quad (29)$$

$$= -\frac{2S(t)\sqrt{d_0}\sqrt{\mu}}{1+\sqrt{\mu}} + B'\mu \quad (30)$$

where $B' = (B + \alpha - \beta)$.

The coefficient, $\gamma_{\text{H}}\gamma_{\text{HCO}_3}$, cannot be separated further but the possibility of computing m_{H} in these solutions deserves careful consideration.

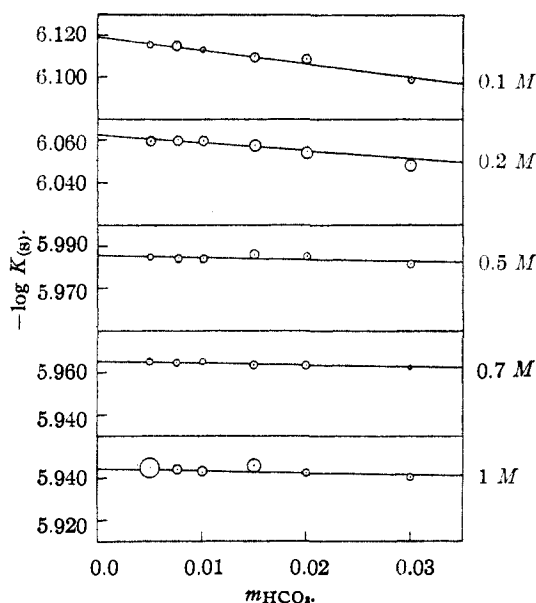


Fig. 2.—Extrapolations at various salt concentrations at 25°.

The Degree of Validity of Computations of the Hydrogen Ion Concentration in Solutions Containing Both Sodium Bicarbonate and Chloride.

—So far, we have adhered strictly to exact procedures which lead to the evaluation of the ionization, $K_{(s=0)}$ and $K_{(s)}$, in pure water and pure sodium chloride solutions, respectively, since these quantities have been extrapolated to zero bicarbonate molality. The question as to what extent these quantities and subsequently m_{H} can be calculated in solutions containing carbon dioxide, sodium bicarbonate and sodium chloride can only be answered by further examination of the data. All the evidence obtained by Harned and Davis indicates that $K_{(s=0)}$ remains constant

within the experimental error from 0 to 1 atmosphere of carbon dioxide, and consequently the medium effect of carbon dioxide is negligible up to a molality of 0.0773, attained at one atmosphere and 0°.

The effect of the presence of sodium bicarbonate at not too high molality can also be shown to be small. In Fig. 2, extrapolation plots of the right side of equation (5) against sodium bicarbonate concentration at various constant sodium chloride molalities at 25° are shown. We note that all these plots slope downwards. This is to be expected since the ionic strength is increased by the addition of sodium bicarbonate which will cause $K_{(s)}$ to increase, or $[-\log K_{(s)}]$ to decrease. Further, this decrease is greater in the solutions containing less sodium chloride. This is to be expected since the relative change in ionic strength becomes greater as the sodium chloride concentrations decrease. We shall assume that sodium bicarbonate and sodium chloride at a given ionic strength have the same effect upon $[-\log K_{(s)}]$ as sodium chloride alone, and show that this assumption conforms to the present experimental data.

Table IV contains the variations in $[-\log K_{(s)}]$ read from the plots in Fig. 2. These are compared with values computed by equation (23) upon the basis of the above assumption. The

TABLE IV

OBSERVED AND CALCULATED VARIATIONS OF $\log K_{(s)}$ IN SODIUM CHLORIDE AND BICARBONATE SOLUTIONS

m_{HCO_3}	0.01		0.02		0.03	
m_{NaCl}	Δ (obs.)	Δ (calcd.)	Δ (obs.)	Δ (calcd.)	Δ (obs.)	Δ (calcd.)
0.1	0.006	0.0079	0.013	0.0153	0.020	0.0221
.2	.004	.0045	.008	.0083	.011	.0123
.5	.001	.0014	.002	.0027	.003	.0041
.7	.001	.0007	.0015	.0014	.002	.0022
1.0	.000	.0003	.001	.0004	.002	.0006

agreement is quite good through the present concentration ranges of the components, and the calculation can be recommended for evaluation $K_{(s)}$ and subsequently m_{H} . Obviously, such a calculation may be expected to be less valid as the bicarbonate molality is increased, or when the ratio of chloride to bicarbonate molalities decreases. From the present evidence it is safe to assume that the equations will be valid to within 0.003 in $\log K_{(s)}$ if m_{HCO_3} is not greater than 0.05 *M* and that the ratio $m_{\text{Cl}}/m_{\text{HCO}_3}$ is not less than 5.

Summary

1. Electromotive forces of the cells $\text{H}_2, \text{CO}_2 | \text{NaHCO}_3(m_1), \text{NaCl}(m_2), \text{CO}_2(m_3) | \text{AgCl-Ag}$ have been determined at 5° intervals from 0 to 50° and at five constant sodium chloride concentrations.

2. From these the ionization function $m_{\text{H}}\gamma_{\text{HCO}_3}/m_{\text{CO}_2}$ or $K_{(s)}$ has been computed from 0 to 1 *M* sodium chloride concentration.

3. Equations for computing $K_{(s)}$ as a function of temperature are given and by their use, the

thermodynamic functions, ΔF_i^0 , ΔH_i^0 , $\Delta C_{P_i}^0$ and ΔS_i^0 may be evaluated.

4. Equations, valid from 0 to 50° and 0 to 1M, are given by means of which $[-\log K_{(s=0)}]$, $[-\log K_{(s)}]$, $\gamma_H\gamma_{HCO_3}/\gamma_{CO_3}\alpha_{H_2O}$, $\gamma_H\gamma_{HCO_3}$, γ_{CO_3} ,

and m_{CO_3} may be calculated. Estimations of the accuracy of these computations in solutions containing both sodium bicarbonate and chloride have been made.

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Hypochlorites in Organic Oxidations

BY JOHN WEIJLARD

The shortage of permanganates during the past few years prompted the investigation of the possibility of utilizing hypochlorites as oxidizing agents in the production of important compounds. Accordingly, it was found that in the production of Vitamin C, diacetone-levo-sorbose which generally is oxidized to diacetone-2-keto-levo-gulonic acid by potassium permanganate¹ could be oxidized in the same yields using alkaline hypochlorites. This method is economical and has other advantages such as freedom from oxalic acid formation and greater simplicity of handling.

Oxidations of aromatic amino sulfides and sulfonates to sulfones in acetic acid solutions are also suitable reactions for hypochlorites. The oxidations of sulfides and sulfoxides to sulfones are generally carried out with nitric acid, chromic acid, and hydrogen peroxide. Phenyl, benzyl and aliphatic sulfides are also oxidized to sulfones by hypochlorites in alkaline solution,² but acetylated aminophenyl sulfides or sulfoxides could not be cleanly oxidized to sulfones by this method, probably because chloramines tend to form under these conditions.³ In acetic acid solutions, the sulfides and sulfoxides could be oxidized to the sulfones by hypochlorites in high yields and without the formation of chlorinated by-products.

A third type of oxidation to which hypochlorites readily lend themselves entails the cleavage of two heterocyclic rings at the carbon-carbon linkage. Nicotine could thus be oxidized to nicotinic acid in yields high by comparison with other oxidizing agents such as nitric acid, chromates, and permanganates. In the same manner 4-amino-5-(3-pyridyl)-pyrazole⁴ was oxidized to nicotinic acid with hypochlorite.

Compounds such as quinoline and quinoxaline were not oxidized to the desired carboxylic acids under the described experimental conditions; the same held true concerning alkyl substituted pyridines.

(1) Reichstein and Grüssner, *Helv. Chim. Acta*, **17**, 321 (1934); U. S. Patent 2,301,811.

(2) Wood, Lowry and Faragher, *Ind. Eng. Chem.*, **16**, 1116 (1924); Wood and Graves, *This Journal*, **50**, 1226 (1928); Birch and Norris, *J. Chem. Soc.*, 1934 (1925).

(3) Willstätter and Mayer, *Ber.*, **37**, 1494 (1904).

(4) Gough and King, *J. Chem. Soc.*, 2968 (1931).

Experimental

Oxidation of Diacetone-levo-sorbose with Hypochlorite.

—Fifty-six grams of chlorine was dissolved in a cold solution of 80 g. of sodium hydroxide in 750 cc. of water. To this freshly prepared hypochlorite solution was added a solution of 50 g. of diacetone-levo-sorbose in 250 cc. of water, followed by 2 g. of nickel chloride in a little water. The mixture was warmed to 50° when a vigorous reaction set in. The temperature was held between 50–60° by occasionally immersing the flask in an ice-bath. After a reaction time of twenty minutes practically all available chlorine was consumed. The catalyst was filtered off and the solution was neutralized with hydrochloric acid, then concentrated *in vacuo* to 350 cc. To the ice cold neutral solution was added 25 cc. of cold concentrated hydrochloric acid, the precipitated diacetone-2-keto-levo-gulonic acid was collected on a filter, washed with ice water, and the yield of anhydrous product estimated to be about 47.5 g. (90%).

Because of the difficulty in drying this acid without partial hydrolysis, a sample for analysis was prepared by dissolving some of the moist product in acetone (saturated solution), adding one volume of ether followed by two volumes of petroleum ether. The precipitated acid was filtered off, washed with petroleum ether and air dried; m. p. 101–102°.

Anal. Calcd. for $C_{12}H_{18}O_7 \cdot H_2O$: C, 49.29; H, 6.90. Found: C, 49.18; H, 6.84.

To further check the yield, the diacetone-2-keto-levo-gulonic acid (47 g.) was directly hydrolyzed and simultaneously rearranged to Vitamin C and isolated as such by known methods⁵; yield, 22.0 g. (73%); m. p. 189.5–190°.

Anal. Calcd. for $C_8H_8O_6$: C, 40.90; H, 4.82. Found: C, 40.87; H, 4.76. No chlorine could be detected.

Oxidation of Sulfides and Sulfoxides to Sulfones with Hypochlorite: 4,4'-Diacetyldiaminodiphenylsulfide.

—Fifty grams of chlorine was dissolved in a cold solution of 75 g. of sodium hydroxide in 1000 cc. of water. To 20 g. of 4,4'-diacetyldiaminodiphenylsulfide dissolved in 500 cc. of hot glacial acetic acid was added in a rapid stream 200 cc. of the prepared hypochlorite solution at 80°, or sufficient hypochlorite solution to produce a slight excess of free chlorine. The reaction mixture was diluted with 2000 cc. of water; the sulfone which precipitated out was collected on a filter, washed with water and dried; yield 22.0 g. of 4,4'-diacetyldiaminodiphenylsulfone (100%); m. p. 289–289.5°.

Anal. Calcd. for $C_{15}H_{16}O_4N_2S$: C, 57.80; H, 4.85; N, 8.43. Found: C, 57.72; H, 4.90; N, 8.35. No chlorine could be detected.

4,4'-Diacetyldiaminodiphenylsulfoxide oxidized as above gave 84% yield of sulfone; m. p. 290–290.5°.

Anal. Found: C, 57.50; H, 4.85; N, 8.70.

Oxidation of Nicotine and Nicotine-like Compounds with Hypochlorite: (a) Nicotine.

—Seventy grams of chlorine was dissolved in a mixture of 600 g. of ice and 400 g. of

(5) U. S. Patents 2,189,830, 2,190,167.