pronounced in the case of $CrICl_2$ and $CrIBr_2$. '*a*' is effectively determined by the Cr–X (and Cr–Y) distance whereas '*c*' is also dependent on the closeness of packing of the halogen layers.

The structure and composition of $CrBrCl_2$ does not change within experimental error on sublimation in high vacuum at 700°. This has been determined by comparison of powder patterns and analyses of samples subjected to successive partial sublimations (*i.e.*, only a fraction of the material was sublimed away). The powder data obtained from the product formed by direct reaction of bromine with $CrCl_2$ at 500° are rather incomplete, presumably because of small particle size. Although poor definition and low intensity made measurement of this pattern difficult, the spacings were identical (within experimental error) with those obtained after sublimation of the samples. The data in Table I were taken from a sublimed sample.

A comparison of powder patterns obtained from $CrBrCl_2$ formed by bromination of chromium(II) chloride with those of other mixtures formed by mixed sublimation of $CrCl_3$ and $CrBr_3$ suggests that all these substances are part of the same system, and that $CrBrCl_2$ is equivalent to a solid solution of $CrCl_3$ and a hypothetical $CrBr_3$ having the same structure. The cell constants observed for the mixtures are shown in Table II, and the relationship of these data to corresponding values for $CrCl_3$, $CrBrCl_2$ and $CrBr_3$ is illustrated in Fig. 1. It is observed from the irregularity in '*c*' that the transition from the $CrCl_3$ type structure to the $CrBr_3$ structure occurs between 0.65- and 0.78-mole fraction of bromide. No irregularity appears in '*a*'. It is planned to investigate this composition range in more detail to determine if this change is associated with the possible compound $CrBr_2Cl$. Thermal instability of similar mixtures involving iodine made it impractical to study the iodide systems by the sublimation technique.

TABLE II

CELL DIMENSIONS OBSERVED FOR SUBLIMED MIXTURES OF $CrCl_3$ AND $CrBr_3$

Effective mole fraction bromide	"*a*"	"*c*"	Av. dev. of *d*calc. from *d*obs., %
0.55	6.149	18.08	0.26 (14 lines obsd.)
.65	6.183	18.19	.44 (10 lines obsd.)
.78	6.225	18.19	.49 (12 lines obsd.)

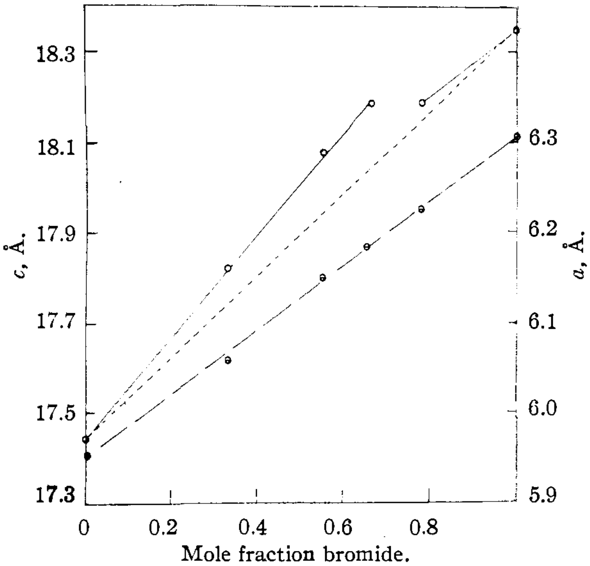

Fig. 1.—Variation of unit cell parameters with composition in the $CrCl_3$-$CrBr_3$ system: ⊖— —, *a*; O==, *c*.

There is no apparent explanation for the change in the nature of the packing of halogens in the bromide rich crystals, particularly in view of the similarity between $CrCl_3$ and CrI_3.

SEATTLE, WASHINGTON

RECEIVED JULY 16, 1951

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

A Polarographic Study of the Kinetics of the Ring → Aldehydo Transformation for Various Aldoses

BY PAUL DELAHAY AND JACOB E. STRASSNER[1]

Polarographic waves of arabinose, xylose, galactose, mannose and dextrose in buffer solutions of *p*H 6.5 to 9.5 are studied in the 0–70° range. Limiting currents are entirely controlled by the rate of the ring → aldehydo transformation. Experimental data are interpreted quantitatively. The same energy of activation 16.5 ± 0.5 kcal. is involved in the rupture of the ring structure of all the aldoses. The entropies of activation are low (less than 10 cal. deg.$^{-1}$) and positive. An equation giving the influence of temperature on limiting currents controlled by rate of reaction and by diffusion is derived.

From their investigation of the polarographic behavior of various aldoses Heyrovsky and Smöler[2] concluded that these substances are not reduced at the dropping mercury electrode. This conclusion, however, had to be revised after Cantor and Peniston[3] obtained polarographic waves with various aldoses at concentrations of the order of 0.1 molar. Even at these relatively high concentrations only rather low limiting currents were observed. This was explained by assuming that the aldehydo form of an aldose is in equilibrium with a much larger amount of the ring form. Only the aldehydo form would be reducible and consequently low limiting currents would be observed even at high concentrations of aldose. The validity of this interpretation was already questioned by Kolthoff and Lingane[4] in 1941, and more recently it was shown by Wiesner[5] that the conclusions of Cantor and Peniston had to be modified. Wiesner observed

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[1] From a thesis to be submitted by J. E. Strassner to the Graduate School of Louisiana State University in partial fulfillment of the requirements for the degree of Master of Science.

[2] J. Heyrovsky and I. Smöler, *Collection Czechoslov. Chem. Communs.*, **4**, 521 (1932).

[3] S. M. Cantor and D. P. Peniston, THIS JOURNAL, **62**, 2113 (1940).

[4] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers Inc., New York, N. Y., 1941, p. 358.

[5] K. Wiesner, *Collection Czechslov, Chem. Communs.*, **12**, 64 (1947).

that the height of all the aldose waves he studied did not vary with the head of mercury. On the basis of this observation Wiesner concluded that the limiting current was proportional to the power $^2/_3$ of the drop weight, *i.e.*, proportional to the power $^2/_3$ of the product of the rate of flow of mercury (m) by the drop time (τ). Furthermore, it was concluded that the limiting current was not determined by the rate of diffusion of the aldehydo form toward the mercury drop, but rather by the rate of the ring → aldehydo transformation at the surface of the mercury drop. Finally, the proportionality of the wave height with $m^{2/3}\tau^{2/3}$ indicates that the equilibrium concentration of the aldehydo form is negligible. Wiesner did not make a thorough study of the kinetics of the ring → aldehydo transformation, and consequently the present investigation was undertaken.

Influence of Temperature on Polarographic Currents Controlled by Rate of Reaction and by Diffusion

The results reported in this paper were interpreted on the basis of a theory of polarographic currents controlled by rate of reaction and by diffusion,[6] which was recently developed in this Laboratory. Since an important part of the present work deals with the influence of temperature on aldose waves, we shall first derive an equation for the temperature coefficient of polarographic currents controlled by rate of reaction and by diffusion. By differentiating with regard to temperature the equation for the instantaneous current previously reported,[6] one obtains

$$\begin{aligned}\frac{1}{i}\frac{\mathrm{d}i}{\mathrm{d}T} &= \frac{1}{P}\frac{\mathrm{d}P}{\mathrm{d}T} + \frac{2}{3m}\frac{\mathrm{d}m}{\mathrm{d}T} + \frac{2}{3t}\frac{\mathrm{d}t}{\mathrm{d}T} + \frac{1}{C}\frac{\mathrm{d}C}{\mathrm{d}T} \\ &+ \frac{\mathrm{d}K}{\mathrm{d}T}\left[\frac{1}{K} + \frac{2Kt}{D} - \frac{2t^{1/2}}{\pi^{1/2}D^{1/2}}\,\frac{e^{-\frac{K^2t}{D}}}{1-\phi\left(\frac{Kt^{1/2}}{D^{1/2}}\right)}\right] \\ &+ \frac{\mathrm{d}D}{\mathrm{d}T}\left[\frac{Kt^{1/2}}{\pi^{1/2}D^{3/2}}\,\frac{e^{-\frac{K^2t}{D}}}{1-\phi\left(\frac{Kt^{1/2}}{D^{1/2}}\right)} - \frac{K^2t}{D}\right] \qquad (1)\end{aligned}$$

in which P is a constant equal to 1255 at 25°, m is the rate of flow of mercury in mg. sec.$^{-1}$, t is the time in sec., of the life of the drop at which the current is measured, C is the concentration, in millimoles per liter, of the substance which is transformed into a reducible species, D is the diffusion coefficient of that substance in cm.^{2} sec.$^{-1}$, K is the rate constant for the transformation yielding the reducible species in cm. sec.$^{-1}$, T is the temperature, and $\phi\left(\frac{Kt^{1/2}}{D^{1/2}}\right)$ represents the error integral $\frac{2}{\pi^{1/2}}\int_0^{\frac{Kt^{1/2}}{D^{1/2}}} e^{-z^2}\,\mathrm{d}z$.

As in the case of a current entirely controlled by diffusion, it can be shown[7] that the sum of the first four terms of the second member of equation (1) is approximately equal to 0.003 deg.$^{-1}$.

When the limiting current is essentially rate controlled, equation (1) becomes

$$\frac{1}{i}\frac{\mathrm{d}i}{\mathrm{d}T} \approx 0.003 + \frac{1}{K}\frac{\mathrm{d}K}{\mathrm{d}T} \qquad (2)$$

which shows that the temperature coefficient of the current is practically equal to the temperature coefficient of the rate of the chemical process. In the case of diffusion control, the second member of equation (1) becomes $0.003 + \frac{1}{2D}\frac{\mathrm{d}D}{\mathrm{d}T}$. This result is in agreement with the temperature coefficient derived from the Ilkovic equation.[7]

In case of rate control, the equation for the average limiting current may be simplified to

$$i_{\text{average}} = 0.60 \times 1255nm^{2/3}\tau^{2/3}KC \qquad (3)$$

in which i is in microamperes, n is the number of electrons involved in the electrode process, τ is the drop time in sec. Equation (3) is valid for a temperature of 25°; at other temperatures the numerical coefficient 1255 should be corrected (see above). Equations (2) and (3) are applicable to the aldose waves which were studied in this paper.

Experimental

Waves were recorded with a Sargent polarograph model XXI. An H-cell[8] with a saturated calomel electrode was used throughout the work. This cell was completely immersed in a constant temperature bath, and the mercury column above the cell was partially immersed in the bath. The temperature was controlled within ±0.03° from 25 to 40°, and at ±0.1° at the other temperatures. In the study of the temperature, the rate of flow of mercury in a phosphate buffer of *p*H 7.75 (see below) at 30.0° was 1.986 mg. sec.$^{-1}$ for a head of mercury of 572 mm. and with the dropping mercury electrode at −1.775 volts (*vs.* S.C.E.). In the study of the influence of *p*H and concentration of aldose a second capillary was used; m was 2.345 mg. sec.$^{-1}$ at −1.819 volts (*vs.* S.C.E.) and for a temperature of 35.0°, all other conditions being the same as with the first capillary. Differences of potentials were measured with a Leeds and Northrup student potentiometer. *p*H values were determined with a Beckman *p*H-member model G, which was standardized with a saturated solution of monopotassium tartrate.[9] Buffer mixtures were prepared according to Britton.[10] Fresh solutions of aldose were prepared each day in order to avoid any fermentation of the sugar.

The aldoses were obtained from the following sources: dextrose, Mallinckrodt; mannose, City Chemical Co., New York; *d*(+)-galactose and *l*(+)-arabinose, Eastman Kodak Co.; *d*(+)-xylose and *d*(−)-arabinose, Pfanstiehl Chemical Co. It was not indicated by the manufacturer whether the mannose was the dextro or the levo form. This, however, is unimportant since the rate of the ring → aldehydo transformation seems to be the same for the dextro and levo forms (see below).

The aldoses were dried at about 100° for at least three hours before weighing.

Description of Results

Description of Waves.—Tracing of typical waves for the five aldoses studied are shown in Fig. 1. Similar waves were obtained in the range 0–70°.

Influence of Temperature.—Aldose waves in a phosphate buffer of *p*H 7.75 were recorded at several temperatures. This phosphate buffer of *p*H 7.75 was selected because its *p*H is practically independent of temperature in the range 0–70°.[10] The corresponding rate constants were calculated

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(6) P. Delahay, THIS JOURNAL, **73**, 4944 (1951).

(7) Reference 4, pp. 74–76.

(8) J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

(9) J. J. Lingane, *Anal. Chem.*, **19**, 810 (1947).

(10) H. T. S. Britton, "Hydrogen Ion," Vol. **1**, D. Van Nostrand Co., New York, N. Y., 1943, p. 307.

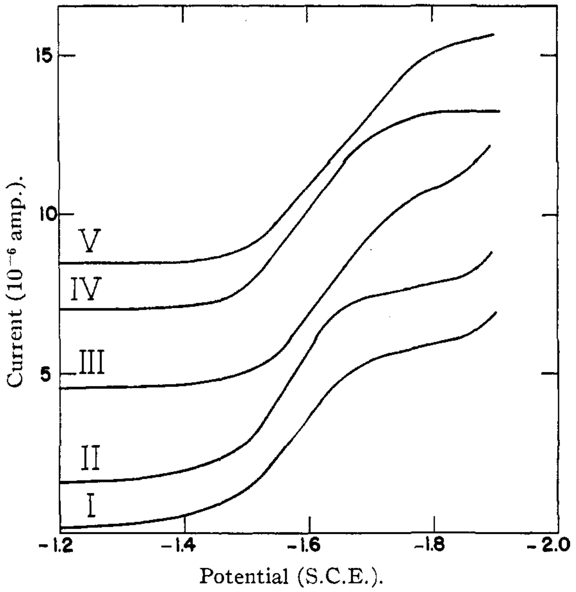


Fig. 1.—Polarographic waves of aldoses in phosphate buffer of *p*H 7.75: I, 0.5 *M* dextrose at 40.2°; II, 0.5 *M* mannose at 39.8°; III, 0.5 *M* galactose at 40.0°; IV, 0.5 *M* xylose at 40.0°; V, 0.5 *M* arabinose at 39.9°. Current is to be multiplied by the following factors: I × 1, II × 2, III × 3, IV × 8 and V × 9. Waves are shifted arbitrarily along the vertical axis.

by application of formula (3) in which the numerical coefficient, *m*, and *C* were corrected for temperature.[7] The drop time was measured for each wave with the dropping mercury electrode at a potential corresponding to the upper plateau of the wave. Logarithms of the rate constant are plotted against the reciprocal of the absolute temperature in Fig. 2. The data for Fig. 2 were obtained with solutions 0.5 molar in aldose.

The influence of temperature was studied for 0.1 molar xylose and 0.1 molar galactose in the same buffer of *p*H 7.75. The corresponding log *K* *vs.* 1/*T* lines were parallel to those of Fig. 2, but the values of *K* were slightly different. At 25° for example, values of $K = 4.07 \times 10^{-6}$ and $K = 3.47 \times 10^{-6}$ cm. sec.$^{-1}$ were obtained for the 0.1 and 0.5 *M* galactose solutions, respectively; for xylose at 25°, $K = 6.31 \times 10^{-6}$ and $K = 7.66 \times 10^{-6}$ cm. sec.$^{-1}$ with the 0.1 and 0.5 *M* solutions, respectively.

The influence of temperature was also studied for 0.5 molar mannose in a phosphate buffer of *p*H 6.60 and for dextrose at *p*H 7.20. The resulting log *K* *vs.* 1/*T* lines were parallel to those of Fig. 2.

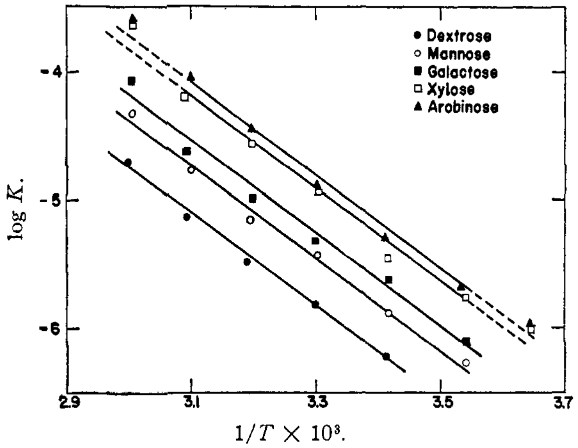


Fig. 2.—Variations of the logarithm of the rate constant for the ring → aldehydo transformation with the reciprocal of absolute temperature. Aldose in phosphate buffer of *p*H 7.75. (*l*(+)-Arabinose used in this study.)

Influence of *p*H.—Waves were recorded at a temperature of 35.0° for various *p*H. Corresponding values of the logarithm of the rate constant are plotted against *p*H in Fig. 3. The concentrations of aldose are as follows: arabinose and xylose, 0.1 molar; dextrose, galactose and mannose, 0.5 molar. The proportionality of the limiting current with the $^2/_3$ power of the drop weight, was verified for each *p*H by recording the wave at two heads of mercury (572 and 717 mm.). Practically the same wave height was observed in all cases, although a slightly smaller wave was observed in some cases with the highest head of mercury. The decrease in wave height never exceeded 7.8% of the limiting current for the lowest head of mercury. However, in most cases the decrease in the limiting current did not exceed 2 to 3%. Since this was rather a minor effect, this phenomenon was not investigated any further. It should be pointed out that this effect of a change in the head of mercury is in the opposite direction of the variation which would be expected if the limiting current were partially diffusion controlled. All results were calculated from the data obtained with a head of mercury of 572 mm.

Discussion of Results

It has been previously reported[6] that a limiting current is essentially rate controlled when the product $KD^{-1/2}$ is smaller than, or equal to, 0.05 sec.$^{-1/2}$. It can be shown that this condition is fulfilled for all the aldose waves studied here, by

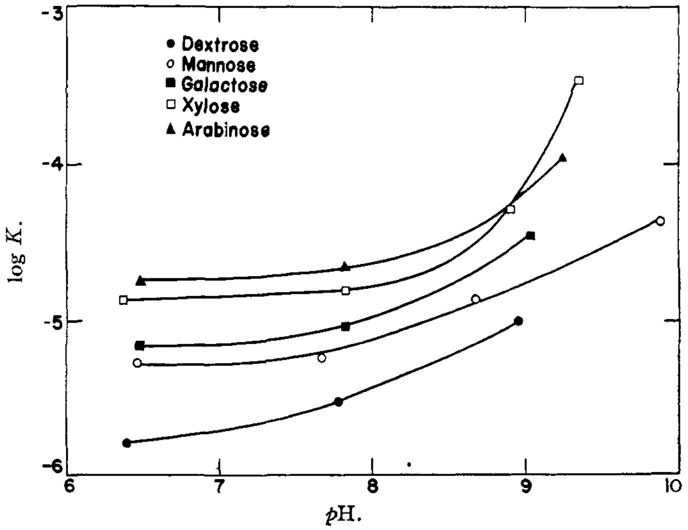


Fig. 3.—Variations of the logarithm of the rate constant for the ring → aldehydo transformation with *p*H at 35°. (*d*(−)-Arabinose was used in this study.)

calculating $KD^{-1/2}$ for the *largest value* of K which was encountered Taking K equal to 1.9×10^{-4} cm. sec.$^{-1}$ (see Fig. 2) and using the approximate value of 10^{-5} cm.^{2} sec.$^{-1}$ for D, one obtains the *maximum* value $KD^{-1/2} = 0.06$ sec.$^{-1/2}$.

Rate Constants for the Ring → Aldehydo Transformation in Solution.—The rate constants calculated thus far correspond to the ring → aldehydo transformation at the surface of the electrode. It is possible to obtain approximate values of the rate constant K_s for the ring → aldehydo transformation *in solution* by dividing the values of K, previously obtained, by the thickness δ of a monolayer of aldose.[6] By taking δ as equal to the average distance between two molecules of aldose in solution, one obtains the values of K_s listed in Table I. Since the introduction of the quantity δ is somewhat artificial, the values of Table I should be considered only as representing an order of magnitude. Nevertheless, those values are of interest since they show that the ring → aldehydo transformation is indeed "very rapid." The rate constants for the aldehydo → ring transformation cannot be calculated from the data of Table I because the equilibrium concentrations of the aldehydo form are not known. However, it can be concluded that the rate constants for the aldehydo → ring transformation are much larger than those for the opposite process since the equilibrium concentrations of aldehydo form are extremely small (see above).

TABLE I

RATE CONSTANTS AND ENTROPIES OF ACTIVATION AT 25° FOR 0.5 MOLAR ALDOSE SOLUTIONS AT pH 7.75.

Aldose	K_s, sec.$^{-1}$	$\Delta S^{\ddagger}$, cal. deg.$^{-1}$
Arabinose	65.5	5.7
Xylose	52.0	4.7
Galactose	23.2	3.4
Mannose	14.7	2.3
Dextrose	6.40	0.6

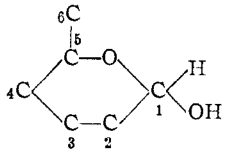
Energy and Entropy of Activation.—Since the log K *vs.* $1/T$ lines of Fig. 2 are essentially parallel, the energy of activation $\Delta H^{\ddagger} = 16.5 \pm 0.5$ kcal. for the ring → aldehydo transformation is practically the same for all the aldoses which were studied here. Furthermore this energy of activation is independent of the pH of the solution of aldose.

Since the pyranose form exists predominantly in solution, one concludes that the energy of activation needed to break the pyranose ring is 16.5 ± 0.5 kcal. The log K *vs.* $1/T$ plots for arabinose and xylose exhibit a slight curvature (Fig. 2) which is probably caused by the presence in solution of the furanose form at an appreciable concentration. The energy of activation for the rupture of the furanose form is probably different from the above value of 16.5 kcal.; and since the ratio of the concentrations of both forms varies with temperature, the log K *vs.* $1/T$ plot is not linear.

The entropy of activation for the opening of the pyranose ring of a given aldose at a given pH can be calculated from the above data by applying the theory of absolute rates[11] and by separating the free energy of activation into the corresponding energy and entropy terms (Table I). The following two conclusions can be drawn from Table I: (1) The entropies of activation are low, as one would expect for a unimolecular process; (2) the entropies of activation are positive as could be expected for a process involving the opening of a ring, *i.e.*, the change to a higher state of disorder. The data of Fig. 3 were analyzed in the same manner and the values of $\Delta S^{\ddagger}$ thus obtained were all positive and comprised between 0 and 9.3 cal. deg.$^{-1}$ (for 35°). These values confirm the above conclusions.

It should be added that in the above calculations of $\Delta S^{\ddagger}$, the energy of activation $\Delta H^{\ddagger}$ has been identified with the energy obtained from the log K *vs.* $1/T$ plot; this is an assumption which is very often made in kinetics studies.

Influence of pH.—In the ring form of an aldose molecule the bond between the oxygen and hydrogen of the hydroxyl group attached to carbon 1 is slightly ionic.[12] Consequently, the bond strength between the oxygen and hydrogen atoms of this hydroxyl group is weakened as the pH increases. Likewise, it is seen from Fig. 3 that the rate of the ring → aldehydo transformation increases rapidly with pH. Therefore, it can be assumed that one of the steps in the activation process for the transformation of the ring structure to the aldehydo form is the removal of the hydrogen ion of the hydroxyl group attached to carbon 1. The removal of this hydrogen atom would cause a rupture of the ring between the oxygen atom of the ring and carbon 1. Furthermore, the rate of the ring → aldehydo transformation is larger for pentoses than for hexoses. This is probably related to the fact that a -CH_2OH group is attached to carbon 5 in hexoses, whereas a hydrogen atom is attached to carbon 5 in pentoses.



Rate for Dextro and Levo Forms.—The rate constant obtained under identical conditions seems to be the same for the dextro and levo forms. This conclusion is based on the following data obtained with arabinose: at pH 7.75 and for a temperature of 35.0°, $K = 2.0 \times 10^{-5}$ cm. sec.$^{-1}$ and $K = 1.9 \times 10^{-5}$ cm. sec.$^{-1}$ for the dextro and levo form, respectively (data from Fig. 2 and 3).

Conclusion

The kinetics of the ring → aldehydo transformation in aldoses can be conveniently studied by the polarographic method, whereas no other approach to this problem has been reported thus far. Furthermore, the present investigation is an applica-

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(11) S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Company, Inc., New York, N. Y., 1941, p. 417.

(12) A. R. Day, "Electronic Mechanisms of Organic Reactions," American Book Company, New York, N. Y., 1950, p. 174.

tion of the theory of polarographic currents controlled by rate of reaction and by diffusion.

Acknowledgment.—This work is part of the project NR 051-258 carried out at Louisiana State University under contract with the Office of Naval Research. The authors are indebted to Dr. C. R. McLellan for helpful comments on possible mechanisms of the ring → aldehydo transformation.

BATON ROUGE, LA. RECEIVED AUGUST 13, 1951

[CONTRIBUTION FROM THE INSTITUTE FOR THE STUDY OF METALS, THE UNIVERSITY OF CHICAGO]

The Extraction of Ferric Chloride by Isopropyl Ether. III[1]

BY NORMAN H. NACHTRIEB AND ROBERT E. FRYXELL[2]

Stoichiometric activity coefficients have been determined by an e.m.f. cell method for ferric chloride in 5 F HCl saturated with $FeCl_2 \cdot 4H_2O$. On the basis of these measurements it is concluded that the abnormal extraction of ferric chloride by isopropyl ether is the result of low activity coefficients for the salt in the ether phase. The appearance of a third liquid phase is shown to arise from the same cause.

Two interpretations have been offered to account for deviations from the Nernst distribution law shown by the ferric chloride:isopropyl ether extraction system. Kato and Ishii[3] and Swift and co-workers,[4,5] on the one hand, have maintained that the iron-bearing compound extracted by ethers undergoes polymerization as the aqueous ferric concentration is increased. The latter investigators assumed essentially ideal behavior of ferric chloride in the aqueous phase and calculated effective polymerization numbers for the ethereal iron complex. Their isopiestic measurements, made on ethereal iron solutions, supported this view although the experiments were only semi-quantitative. Nachtrieb, Fryxell and Conway,[6,7] on the other hand, have proposed that deviations of the aqueous ferric chloride phase from dilute solution laws may be responsible for the apparent failure of the distribution law. This proposal was based primarily upon the adherence of absorption bands of the ethereal solutions to Beer's law over a range of iron concentration which extended well into the region of anomalous extraction.

A choice between these opposing interpretations can be made by measurement of some thermodynamic property of ferric chloride in either phase as a function of the concentration of trivalent iron in that phase. Isopiestic experiments reach equilibrium only slowly and are difficult to interpret in a 4-component system (ferric chloride, hydrogen chloride, water and isopropyl ether) when three of the components are volatile. The authors have therefore attempted to determine the variation in the activity coefficient of ferric chloride in the aqueous phase by an e.m.f. method. In order to do this it has been necessary to introduce a fifth component (ferrous chloride) into the system to permit the use of a cell with a ferrous ferric electrode. Although the system has been made more complex thereby the conclusions drawn are believed to apply to the simpler extraction system. As will be seen, the stoichiometric activity coefficient of aqueous ferric chloride does not deviate significantly from unity over the concentration range concerned. By implication, then, the cause of the abnormal distribution is a remarkable decrease in the activity coefficient of ferric chloride in the ether phase, in agreement with the interpretation of Swift and his co-workers.

E.m.f. Measurements

The cell studied was

$$Pt/FeCl_2 \cdot 4H_2O/FeCl_{3(xF)} + HCl_{(5F)}/HCl_{(5F)}/Hg_2Cl_2/Hg \qquad (1)$$

corresponding to the cell reaction

$$FeCl_2 \cdot 4H_2O_{(s)} + {}^1/{}_2Hg_2Cl_2 = FeCl_{3(5F\ HCl)} + Hg_{(l)} + 4H_2O$$

Three of the cell components are pure substances ($FeCl_2 \cdot 4H_2O$, Hg_2Cl_2 and Hg) and are therefore at constant activity. The activities of water and of ferrous chloride are not separately fixed, but for the purposes of this experiment probably do not vary appreciably. The activity of $FeCl_2 \cdot 4H_2O$ is constant, but the formal solubility in 5 F HCl at 25° varies with ferric chloride concentration according to the equation: Solubility = $1.75 - 0.85[Fe^{III}]$. This equation gives the ferrous chloride solubility to ± 0.01 F for ferric chloride concentrations up to 0.5 F. Thus, at constant hydrochloric acid activity the e.m.f. of the cell varies with the concentration of ferric chloride according to the equation

$$E = E^0 - \frac{RT}{F} \ln\,[FeCl_3] - \frac{RT}{F} \ln\,\gamma_{FeCl_3}$$

where $[FeCl_3]$ is the stoichiometric ferric iron concentration expressed in formula weights per liter and γ_{FeCl_3} is the stoichiometric activity coefficient for ferric chloride.

Figure 1 shows the cell. The calomel reference electrode (A) made contact with the cell solution through a capillary (B) which was flushed before each experiment with 5.00 F HCl from the reservoir (C). Nitrogen, purified by passage over finely divided copper at 245° was admitted through (G) and removed through (H) to prevent oxidation of ferrous chloride. The temperature was maintained at 25.0 ± 0.1° by circulating thermostated water through the cell jacket. Magnetic stirring ensured thorough mixing of the

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(1) Abstracted from a dissertation submitted by Robert E. Fryxell to the Department of Chemistry of the University of Chicago in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) General Electric Company, Pittsfield, Massachusetts.

(3) S. Kato and R. Ishii, *Sci. Papers Inst. Phys. Chem. Res., Tokyo*, **36**, 82 (1939).

(4) J. Axelrod and E. H. Swift, THIS JOURNAL, **62**, 33 (1940).

(5) R. J. Meyers, D. E. Metzler and E. H. Swift, *ibid.*, **72**, 3767 (1950); R. J. Meyers and D. E. Metzler, *ibid.*, **72**, 3772 (1950); D. E. Metzler and R. J. Meyers, *ibid.*, **72**, 3776 (1950).

(6) N. H. Nachtrieb and J. G. Conway, *ibid.*, **70**, 3547 (1948).

(7) N. H. Nachtrieb and R. E. Fryxell, *ibid.*, **70**, 3552 (1948).