TABLE I

Salt	NiCl₂							CoCl₂			
Vol. in liters/mole salt	4.4	8.8	17.2	35.2							
Moles H_2O/mole salt					2	8	32	16	32		
Molar concentration										0.05	0.01
Temperature, °C.	18	18	18	18	100	85.5	100	25	25	25	25
Hydrolysis, %	0.127	0.16	0.23	0.30	0.013	0.008	0.0019	0.11	0.17	0.12	0.53
$K \times 10^{-5}$	0.36	0.29	0.27	0.36	.....	.....	......	...	...	...	...
Investigator	3	3	3	3	5	5	5	4	4	4	4

TABLE II

HYDROLYSIS OF NICKEL CHLORIDE AT 25°

Mole $NiCl_2$/1000 g. of H_2O	Mole H^+/1000 g. of H_2O	$K_1 = \frac{a_{NiOH^+} \times a_{H^+}}{a_{Ni^{++}}} \times 10^{-11}$	
0.0156	4.6×10^{-7}	3.1	
.0312	5.6×10^{-7}	2.0	
.0625	7.2×10^{-7}	1.7	Calculated from previously published data, 1.5×10^{-11}
.1250	1.0×10^{-6}	1.6	
.250	1.6×10^{-6}	2.0	
.500	2.5×10^{-6}	2.6	
	Average	2.3	

TABLE III

HYDROLYSIS OF COBALT CHLORIDE

Mole of $CoCl_2$/1000 g. of H_2O	Mole H^+/1000 g. of H_2O	$K = \frac{a_{CoOH^+} \times a_{H^+}}{a_{Co^{++}}} \times 10^{-13}$	
0.01	6.5×10^{-8}	5.6	
.02	9.6×10^{-8}	6.6	
.05	1.2×10^{-7}	4.8	Calculated from previously published data. 4.0×10^{-13}
.075	1.7×10^{-7}	7.1	
.1	2.0×10^{-7}	7.5	
	Average	6.3	

precipitating the nickel with alcoholic dimethylglyoxime as recommended by Treadwell and Hall.[7]

The Data.—Data are collected in Tables II and III. The generalized hydrolysis reaction and equilibrium expression for $NiCl_2$ and $CoCl_2$ is

$$M^{++} + HOH \rightleftarrows MOH^+ + H^+$$

$$K = \frac{a_{MOH^+} \times a_{H^+}}{a_{M^{++}}}$$

Conclusion

Hydrolysis Constant

$Ni^{++} + HOH \rightleftarrows NiOH^+ + H^+ \quad K = 2.3 \times 10^{-11}$

$\Delta F^0 = 14000$ cal./mole

$Co^{++} + HOH \rightleftarrows CoOH^+ + H^+ \quad K = 6.3 \times 10^{-13}$

$\Delta F^0 = 17000$ cal./mole

From the magnitude of the hydrolysis constants it can be concluded that $Ni(OH)_2$ and $Co(OH)_2$ are relatively strong bases. The hydrolysis data confirm the results obtained in solubility measurements of $Ni(OH)_2$ and $Co(OH)_2$.

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[7] Treadwell and Hall, "Analytical Chemistry," John Wiley & Sons, Inc., New York City, 9th Ed., 1937–1942.

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

Polarographic Study of the Kinetics of Ionic Recombination and Comparison with Onsager's Theory

BY PAUL DELAHAY AND THOMAS J. ADAMS[1]

An equation for the rate constant of processes involving the recombination of two univalent ions is derived from Onsager's theory of ionic recombination. The temperature coefficient of the rate constant is essentially the same as for a diffusion process. The theoretical results are compared with polarographic data for the recombination of pyruvate and hydrogen ions. The dependence of the rate constant on ionic strength is studied experimentally, and the results are analyzed on the basis of the Debye–Hückel theory. Finally, the influence of the rate of the electrode process in polarographic studies of ionic recombination is discussed quantitatively.

The theory of ionic recombination which was developed by Onsager[2] has been verified by measuring the variations of the dissociation constant of weak electrolytes caused by the application of an electrical field of high intensity.[3] The implications of Onsager's theory with regard to the kinetics of ionic recombination have not been explored possibly because of the lack of an experimental method enabling one to verify the theoretical results. With the recent development of a polarographic method for the study of ionic recombination,[4,5,6] it becomes possible at the present to compare theoretical results on ionic recombination with the corresponding experimental data. Such a comparison is the object of the present investigation.

Kinetics of Ionic Recombination

Rate Constants for Ionic Recombination Processes.—The rate of recombination dC_{CA}/dt of

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

[2] L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

[3] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Edition, Reinhold Publishing Corp., New York, N. Y., 1950, pp. 216–222.

[4] R. Brdicka and K. Wiesner, *Collection Czechoslov. Chem. Commun.*, **12**, 138 (1947).

[5] J. Koutecky and R. Brdicka, *ibid.*, **12**, 337 (1947).

[6] P. Delahay, THIS JOURNAL, **73**, 4944 (1951). Note that *K* in equation (15) is in cm. sec.$^{-1}$ (moles per cc.)$^{-1}$.

two univalent ions C^+ and A^- which combine into a molecule CA is defined by the equation

$$\mathrm{d}C_{\mathrm{CA}}/\mathrm{d}t = k_r' C_{\mathrm{C}^+} C_{\mathrm{A}^-} - k_d' C_{\mathrm{CA}} \qquad (1)$$

in which k_r' is the rate constant for the recombination process in sec.$^{-1}$ (moles per cc.)$^{-1}$, k_d' is the rate constant for the dissociation process in sec.$^{-1}$, and the C's are the concentrations in moles per cc. An equation for k_r' is obtained by combining the value of the Langevin time lag, expressed as a function of k_r',[7] with the value of the time lag derived[8] from Onsager's theory.[2] By introducing the equivalent conductance at infinite dilution Λ_0 in the resulting equation, one obtains

$$k_r' = 36\pi 10^{11} \frac{\Lambda_0}{d} \qquad (2)$$

in which d is the dielectric constant of the solution.

A different form of equation (2), which is convenient in polarographic studies, is obtained by expressing the equivalent conductance at infinite dilution as a function of the diffusion coefficients of the ions C^+ and A^-.[9] After numerical substitutions one obtains

$$k_r' = 1.26 \times 10^{22} \frac{D_{\mathrm{C}^+} + D_{\mathrm{A}^-}}{Td} \qquad (3)$$

in which D_{C^+} and D_{A^-} are the diffusion coefficients in cm.^{2} sec.$^{-1}$ of ions C^+ and A^-, respectively, and T is the absolute temperature.

Equations (2) and (3) are important because they relate the rate constant k_r' to quantities whose numerical values are available or easily obtainable. Since the diffusion coefficients of all ions, except hydrogen and hydroxyl ions, are of the same order of magnitude at a given temperature, the rate constant k_r' is of the same order for all ionic recombination processes which do not involve hydrogen or hydroxyl ions. Taking $D_{\mathrm{C}^+} = D_{\mathrm{A}^-} = 10^{-5}$ cm.^{2} sec.$^{-1}$, $d = 78.5$ and $T = 298°$, one obtains approximately 10^{13} sec.$^{-1}$ (moles per cc.)$^{-1}$ for the order of magnitude of k_r' at 25°. The rate constants for recombination processes involving hydrogen ion (*i.e.*, recombination of the ions of weak acids) are somewhat larger because the diffusion coefficient of hydrogen ion is about ten times as large as that of other ions.[10]

Influence of Temperature.—By taking the logarithms of both members of equation (3) and by differentiating the resulting equation, one obtains

$$\frac{1}{k_r'}\frac{\mathrm{d}k_r'}{\mathrm{d}T} = \frac{1}{D_{\mathrm{C}^+} + D_{\mathrm{A}^-}} \frac{\mathrm{d}(D_{\mathrm{C}^+} + D_{\mathrm{A}^-})}{\mathrm{d}T} - \frac{1}{T} + 0.0046 \qquad (4)$$

in which -0.0046 is approximately the temperature coefficient of the dielectric constant of water according to Wyman.[11] Since temperature coefficients of diffusion coefficients at room temperature are several times larger than the last term of the second member of equation (4), the temperature coefficient of the rate constant k_r' is essentially the same as for a diffusion process.

The above formulas are verified experimentally in the present paper and some other features of the kinetics of ionic recombination are also discussed.

Polarographic Determination of Rate Constants for Ionic Recombination Processes

The theory of polarographic currents controlled by rate of reaction and by diffusion, which was developed in this Laboratory[6] is applicable to ionic recombination processes. The rate of recombination per unit area at the *surface of the mercury drop* is given by equation (1) in which the term $\mathrm{d}C_{\mathrm{CA}}/\mathrm{d}t$ is replaced by $\mathrm{d}N/\mathrm{d}t$ ($\mathrm{d}N$, number of moles of CA formed at the surface of the mercury drop in time $\mathrm{d}t$) and the rate constants k_r and k_d for heterogeneous processes are substituted to k_r' and k_d'.[6] The rate constants k_r and k_d are expressed in cm. sec.$^{-1}$ (moles per cc.)$^{-1}$ and cm. sec.,$^{-1}$ respectively, in the equation thus obtained. In the theory previously developed[4] it was assumed that the concentration of molecules CA at the surface of the electrode is negligible. Thus, it was assumed that the molecules CA react on the electrode surface as soon as they are formed. This implies that the rate constant for the electrode process involving the molecules CA is much larger than the rate constant for the ionic recombination process. This hypothesis is re-examined here.

Influence of the Rate of the Electrode Process.—In the case of an irreversible electrode process, the rate of electrode reaction is expressed as a function of the rate constant k_e for the electrode process[12] by the equation

$$\mathrm{d}N/\mathrm{d}t = k_e C_{\mathrm{CA}} \qquad (5)$$

in which k_e is in cm. sec.$^{-1}$. By combining equation (5) with the modified equation (1) (see above), one obtains

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{k_r}{1 + (k_d/k_e)} C_{\mathrm{C}^+} C_{\mathrm{A}^-} \qquad (6)$$

Equation (6) is of the same general form as the simplified equation obtained by assuming that k_e is infinite. However, the values of the rate constant which are obtained by application of the theory previously developed are actually the values of $k_r/(1 + (k_d/k_e)$. The resulting error will be appreciable when k_d is not negligible in comparison with k_e. When the wave, whose height is controlled by rate of reaction and by diffusion, exhibits a well defined upper plateau, k_e is very large[12] and the value of k_r need not be corrected. When k_e is not very large the correct value of k_r can be obtained provided that the rate of the electrode process k_e and the dissociation constant of the molecule CA are known. By equating the coefficient $k_r/(1 + (k_d/k_e))$ to the value of the rate constant thus obtained, and by replacing k_d by Kk_r (K dissociation constant in moles per cc.) one obtains an equation in k_r which yields the corrected value of k_r.

Experimental

Waves were recorded with a Sargent polarograph model XII. A conventional erlenmeyer cell was used throughout the work. This cell was completely immersed in a constant temperature bath, and the mercury column above the cell

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(7) Ref. 3, p. 67.

(8) Ref. 3, p. 113.

(9) W. Nernst, *Z. physik. Chem.*, **2**, 613 (1888).

(10) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers Inc., New York, N. Y., 1941, p. 45.

(11) J. Wyman, Jr., *Phys. Rev.*, **35**, 623 (1930).

(12) P. Delahay and J. E. Strassner, THIS JOURNAL, **73**, 5219 (1951).

was partially immersed in the bath. The temperature was controlled at ± 0.03°, from 25 to 40°, and within ± 0.1° at other temperatures. Citric acid–sodium hydroxide and monopotassium phosphate–sodium hydroxide buffers[13] were used. The *p*H's of the buffer mixtures were corrected for temperature according to Britton.[13] *p*H's were measured at room temperature with a Beckman *p*H meter model G, which was standardized with a saturated solution of monopotassium tartrate.[14] In the study of the influence of temperature on the recombination of pyruvate and hydrogen ions, solid potassium nitrate was added to make the final concentration of the solutions under investigation 0.5 molar in potassium nitrate. This was done in order to avoid appreciable variations of the ionic strength with *p*H. In the study of the influence of ionic strength on the rate of recombination of pyruvate and hydrogen ions, the concentrations of the components of the buffer mixtures were only one-tenth of those quoted by Britton,[13] and the ionic strength was adjusted by dissolving solid potassium nitrate. All solutions were prepared from a 0.01 *M* stock stolution of pyruvic acid which was stored at about 0°. This stock solution was prepared by weighing the proper amount of pyruvic acid which had been purified by distillation under vacuum. The rate of flow of mercury, 2.14 mg. sec.$^{-1}$ was measured at 34.0° in a monopotassium phosphate–sodium hydroxide buffer of *p*H 5.90. Values of the rate of flow of mercury at other temperatures were calculated on the basis of the value measured at 34.0°.[15] The diffusion coefficient of pyruvate ion at various temperatures was calculated by means of the Ilkovic equation in which all the terms had been corrected for temperature,[15] except the drop time, which was measured after each recording. The drop time was measured with an applied potential which corresponded to a point of the upper plateau of the first pyruvic wave.

Description and Discussion of Results

Influence of Temperature.—The influence of *p*H on the polarographic behavior of pyruvic acid has been reported by several authors[4–6,16] Below *p*H 4.5, one wave which corresponds to the reduction of the undissociated acid is observed. Above *p*H 4.5 and below *p*H 7 a second wave appears, which corresponds to the reduction of pyruvate ion. Only the latter wave is observed above *p*H 7. It was previously[6] shown that the rate constant k_r for the recombination of pyruvate and hydrogen ions at the *surface of the mercury drop* can be calculated from the *p*H of the solution for which the heights of the first and second waves are equal. Data obtained at different temperatures are listed in Table I. The logarithms of the rate constant k_r and of the diffusion coefficient D_{A^-} of pyruvate ion are plotted against the reciprocal of absolute temperature in Fig. 1.

TABLE I

DATA FOR THE RECOMBINATION OF PYRUVATE AND HYDROGEN IONS AT VARIOUS TEMPERATURES[a]

Temp., °C.	i_∞,[b] microamp.	Drop time, sec.	D_A[c] 10^{-5} cm.^{2} sec.$^{-1}$	$p\mathrm{H}_{1/2}$[d]
2.2	3.43	3.32	0.22	5.75
20.2	4.45	3.11	.36	5.82
34.0	5.50	2.97	.52	5.93
50.5	7.70	2.84	.96	5.98

[a] Concentration of pyruvic acid, 10^{-3} molar. [b] Limiting current of pyruvic acid at *p*H lower than 4 (around 3.7). [c] Diffusion coefficient of pyruvate ion. [d] *p*H of solution for which both pyruvic waves are of equal heights.

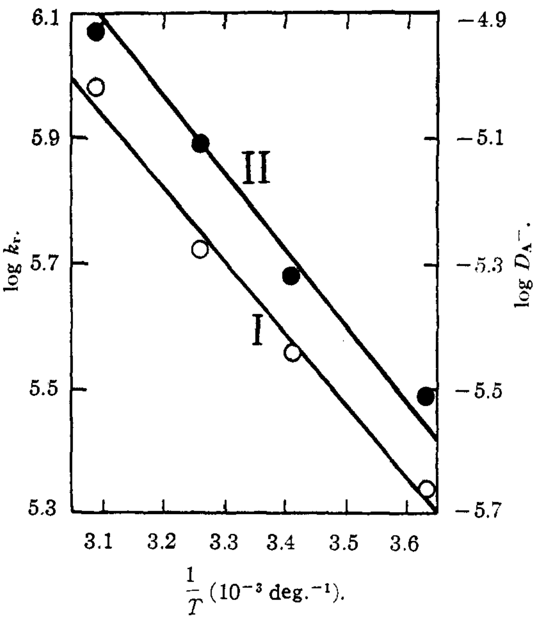

Fig. 1.—Variations of log D_{A^-} (I) and log k_r (II) with the reciprocal of absolute temperature; D_{A^-}, diffusion coefficient of pyruvate ion in cm.^{2} sec.$^{-1}$; k_r rate of recombination of hydrogen and pyruvate ions at the surface of the electrode in cm. sec.$^{-1}$ (moles per cc.)$^{-1}$; II is calculated curve.

From the log D_{A^-} *vs.* $1/T$ plot (curve I), one calculates a free energy of activation of 5.30 kcal. for the diffusion of pyruvate ion. If one assumes that the diffusion coefficients of hydrogen and pyruvate ions vary in the same manner with temperature, it is possible to calculate the curve log k_r *vs.* $1/T$ (curve II), on the basis of equation 3. In the determination of curve II of Fig. 1, the numerical coefficient of equation (3) was changed in order to fit the experimental datum at 34° (see below). It should indeed be recalled that the values of k_r of Fig. 1 correspond to an heterogeneous process at the electrode surface whereas the rate constant of equation 3 is for an homogeneous reaction.

Figure 1 shows that the slopes of the log D_{A^-} *vs.* $1/T$ and log k_r *vs.* $1/T$ lines are essentially the same. This is a conclusion which can be drawn from equation (4). However, the calculated curve log k_r *vs.* $1/T$ (II) is slightly steeper than the average line through the experimental points. This discrepancy is possibly caused by experimental errors since the polarographic values of k_r are undoubtedly affected by several causes of error. Among these, errors in *p*H measurements are particularly detrimental to the accuracy. For example an error of 0.01 *p*H unit in the determination of the $p\mathrm{H}_{1/2}$ affects log k_r by 0.01. Furthermore, the upper plateau of the first pyruvic wave is rather ill-defined,[4] and the resulting errors in the measurement of the limiting current of this wave affect the value of $p\mathrm{H}_{1/2}$. Nevertheless it seems from Fig. 1 that the average line through the experimental points representing log k_r is parallel to curve I. This will be commented upon in the following section.

Comparison with the Rate Constant Calculated from Onsager's Theory.—By using the average

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[13] H. T. S. Britton, "Hydrogen Ions," Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1943, pp. 303, 307.

[14] J. J. Lingane, *Anal. Chem.*, **19**, 810 (1947).

[15] Ref. 10, pp. 74–76.

[16] O. H. Müller and J. P. Baumberger, THIS JOURNAL, **61**, 590 (1939).

experimental value $D_{A^-} = 0.44 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ for pyruvate ion at 25° and $D_{C^+} = 9.3 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ for hydrogen ion,[10] one obtains by application of formula (3) $k_r' = 5.1 \times 10^{13}$ sec.$^{-1}$ (moles per cc.)$^{-1}$. The experimental value of k_r is 5.75 $\times$ 10^2 cm. sec.$^{-1}$ (moles per liter)$^{-1}$ or 5.75 $\times$ 10^5 cm. sec.$^{-1}$ (moles per cc.)$^{-1}$ and the corresponding value of k_r' is $(5.75/\delta)$ 10^5 sec.$^{-1}$ (moles per cc.)$^{-1}$, δ being the average distance of two pyruvate ions in solution. By taking $\delta = 1.28 \times 10^{-6}$ cm. one obtains $k_r' = 4.49 \times 10^{11}$ sec.$^{-1}$ (moles per cc.)$^{-1}$ from the polarographic data. Thus, the polarographic value of k_r' is about one hundredth the value calculated on the basis of Onsager's theory. Such a discrepancy is to be expected since the conditions under which the recombination of ions takes place are very different. The value of k_r' obtained from polarographic data corresponds to a reaction at the surface of the mercury drop where the ions are under the influence of a very high electrical field. On the other hand, the value k_r' derived from Onsager's theory corresponds to a reaction in solution in the absence of any perturbing field. The gradient of potential at the surface of the mercury drop probably exceeds 10^6 volts cm.$^{-1}$[1,17] and under these conditions the dielectric constant calculated by extrapolating Malch's results[17-19] is only a small fraction of the normal value 78.5.[11] This, however, would made the polarographic value of k_r even smaller for $d = 78.5$. Furthermore, it is possible that the temperature coefficient of the dielectric constant in a medium under the influence of a high electric field is much smaller than the normal temperature coefficient which was used in the derivation of formula (4). This would explain why the log k_r *vs.* $1/T$ line of Fig. 1 is practically parallel to the log D_{A^-} *vs.* $1/T$ line. Actually it is quite likely that the above value $k_r' = 4.49 \times 10^{11}$ sec.$^{-1}$ (moles cc.)$^{-1}$ obtained from polarographic data is even too small since the influence of the electrode reaction was neglected (formula 6). However, it is not possible to make a correction since the rate constant for the electrode reaction at the potential at which the wave was measured is not known. Finally, it should be added that the introduction of the quantity δ is somewhat artificial, and that the conversion of k_r to k_r' is only approximate.

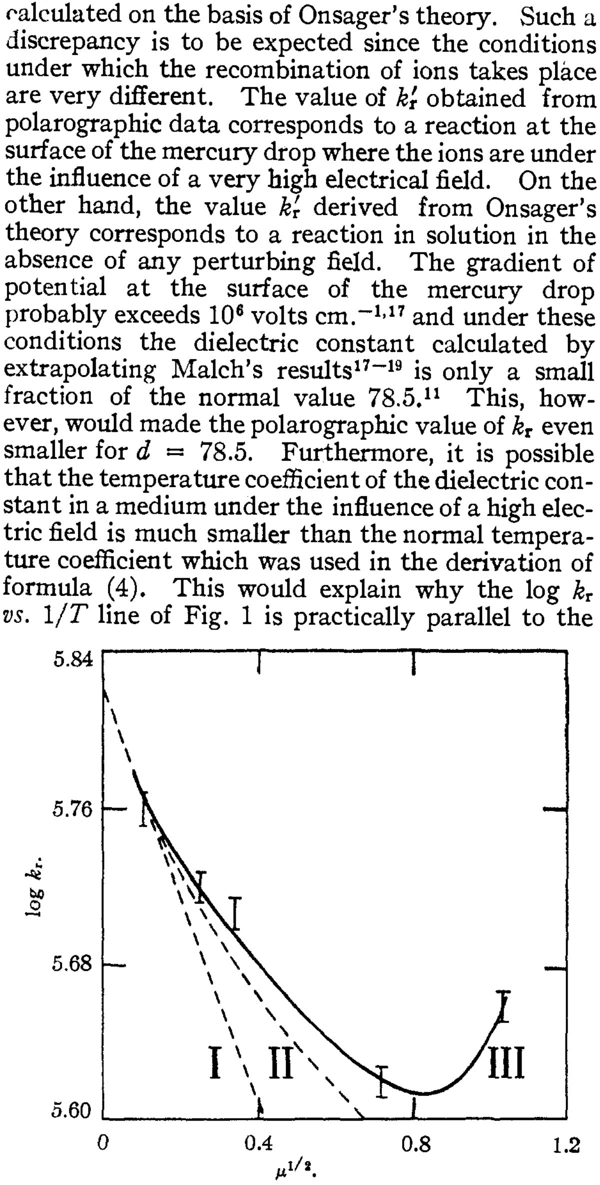

Fig. 2.—Variations of log k_r with the square root of ionic strength: *I*, Debye–Hückel limiting law; II, extended Debye–Hückel law; III, experimental curve. k_r rate of recombination of hydrogen and pyruvate ions at the surface of the electrode in cm. sec.$^{-1}$ (moles per cc.)$^{-1}$.

Rate Constant for the Dissociation of Pyruvic Acid.—An approximate value of the dissociation constant of pyruvic acid was obtained by measuring the *p*H of a 0.05 *M* pyruvic acid solution at 25°. From the value of *p*H 1.98 which was found, the value $K = 2.8 \times 10^{-3}$ mole per liter was calculated. Using this value of K and $k_r = 5.75 \times 10^5$ cm. sec.$^{-1}$ (moles per cc.)$^{-1}$, one calculates $k_d = 1.6$ cm. sec.$^{-1}$. The corresponding value of k_d' is 1.25×10^6 sec.$^{-1}$.

Influence of Ionic Strength.—The influence of ionic strength of the solution was investigated for 10^{-4} molar solutions of pyruvic acid at 34° (Table II); and the logarithms of the rate constant thus obtained are plotted in Fig. 2. The experimental value of the diffusion coefficient $D_{A^-} = 0.525 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ was used in the calculations of k_r. Note that the value of k_r obtained with a 10^{-4} molar solution is somewhat smaller than the previous value obtained with a 10^{-3} molar solution. This matter is being investigated.

TABLE II

DATA FOR THE RECOMBINATION OF HYDROGEN AND PYRUVATE IONS AT 34° IN MEDIA OF VARIOUS IONIC STRENGTHS

Concentration of KNO_3, mole per l.	Ionic strength	$pH_{1/2}$
0	0.011	5.82
0.05	.061	5.78
0.1	.11	5.77
0.5	.51	5.67
1	1.01	5.70

The variations of rate constant at low ionic strengths can be calculated on the basis of the Debye–Hückel theory. Since the values of k_r are automatically corrected for the variations of the activity of hydrogen ion by the *p*H measurements, the rate constant k_r should vary in the same manner as the activity coefficient of pyruvate ion. Therefore, the slope of the experimental curve III of Fig. 2 should be 0.518[20] at $\mu = 0$. Figure 2 shows that this seems to be the case. The agreement between experimental and calculated data is somewhat better if one considers the extended law $0.518\ \mu^{1/2}/(1 + \mu^{1/2})$ (curve II). The increase of log k_r at high ionic strengths is caused by the salting effect. One infers from Fig. 2 that the variations of the rate constant k_r with the ionic strength of the medium can be predicted on the basis of the Debye–Hückel equation at ionic strengths smaller than 0.01. It should be pointed

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[17] D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947), see p. 481.

[18] P. Debye, "Polar Molecules," Chemical Catalog Co., Inc., (Reinhold Publ. Corp.), New York, N. Y., 1929, p. 111.

[19] J. Malch, *Ann. Phys.*, **84**, 841 (1927); also *Z. Physik*, **29**, 770 (1938); **30**, 837 (1929).

[20] Ref. 3, p. 587.

out that the determination of k_r is not very accurate and that the precision on the value of log k_r is probably of the order of ±0.01. Furthermore, the same value of D_{A^-} was used in the calculations of k_r at different ionic strengths, whereas D_{A^-} actually decreases with increasing ionic strength. Measurements at ionic strengths lower than 0.01 were not carried out because it would have been necessary to decrease the concentrations of the buffer mixtures and pyruvic acid to values at which the accuracy of the polarographic measurements becomes too low.

Conclusion.—The agreement between the values of the rate constant for ionic recombination, as obtained by the polarographic method and from Onsager's theory, is fair.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND METALLURGY, NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY, SOCORRO]

The In–In_2S_3 System[1]

BY M. F. STUBBS, J. A. SCHUFLE, A. J. THOMPSON AND J. M. DUNCAN

A phase diagram for the In–In_2S_3 system obtained by thermal analysis, metallographic and X-ray studies is presented. Compounds In_2S_3, (In_3S_4), (In_5S_6) and InS are found to exist, but not the previously reported compound In_2S. The melting point of In_2S_3 is found to be 1090–1100° with decomposition. X-Ray evidence has been obtained to supplement the thermal analysis, and compounds In_2S_3, (In_5S_6) and InS are found to be stable at room temperature.

Data obtained during the determination of equilibrium constants in the reduction of indium trisulfide with hydrogen (work in progress) showed that the In–In_2S_3 system was probably more complex than shown by Thiel and Luckmann[2] in their study of the same system. These authors made visual observations of the melting points and so-called "sintering points" of various mixtures of indium and sulfur. Their results gave limited information about the internal structure of the phase diagram. With indium metal now available in commercial quantities, we have again carried out a thermal analysis of the In–In_2S_3 system, and have supplemented these data with metallographic and X-ray examinations.

Apparatus.—In contrast to Thiel and Luckmann, who used only enough material to fill a capillary melting point tube, we were able to use sufficient material (40–50 g. for each cooling curve) to give sizeable heats of fusion and reaction which could be recorded readily on cooling curves. This required a fairly large melting point tube. The high temperatures (600–1100°) at which the sulfides of indium melt required the use of a tube constructed of high-melting material such as Vycor (96% silica) glass. Metal cannot be used since sulfur reacts with almost any metal at these temperatures. Helium gas at atmospheric pressure was passed over the melt to prevent oxidation. A thermocouple well was imbedded in the melt and sealed into the top of the melting point tube with Sauereisen heat resistant cement.

The high temperatures required were reached quickly and conveniently by use of an Ajax–Northrup Induction Furnace. The Vycor tube containing the material to be melted was placed in a snug-fitting carbon crucible which was heated by induced current.

The temperatures were recorded by means of a chromel–alumel thermocouple and a General Electric thermocouple potentiometer, type P. J. — 1 B 4. The thermocouple was calibrated against the following standards: (1) U. S. Bureau of Standards copper ingot, m.p. 1083.2°; (2) silver foil, 99.9975% Ag, m.p. 960.5°; (3) 28.1% copper, 71.9% silver alloy, which gives a eutectic melting at 779°; (4) antimony, 99.8–99.83% Sb, m.p. 630.5°; and (5) zinc, 99.98% Zn, m.p. 419.4°.

The space between the carbon crucible and the induction coil in the induction furnace was packed with calcium oxide as an insulating material to slow down the rate of cooling.

Preparation of Materials Used.—The best method for preparing pure In_2S_3 proved to be that of precipitation from aqueous solution. Pure indium metal (99.96+% indium) was dissolved in hydrochloric acid and the excess acid evaporated off on a hot plate. The resulting solid $InCl_3$ was dissolved in water, the *p*H of the solution adjusted to approximately 3, and pure hydrogen sulfide gas from a cylinder was bubbled through it. It was found necessary to maintain the *p*H of the solution between 1.5 and 3.0. This was done by dropwise addition of a 3.0 *M* solution of ammonium acetate. In_2S_3 will not precipitate at *p*H values below 1.5, while at *p*H values above 3.4, there is danger of contamination with hydrous indium oxide.[3] The orange-yellow precipitate of In_2S_3 was washed by decantation, filtered, washed with H_2S water and dried in an oven for several hours at 130°. The sulfide was then pulverized in an agate mortar, digested with hot water, filtered, washed and dried overnight at 130°. The sulfide finally was heated in a vacuum or atmosphere of H_2S at approximately 350° for at least an hour to remove traces of ammonium salts, sulfur and water. In_2S_3 prepared by this method gave the following typical analyses after conversion to hydroxide and ignition to oxide at 800°: In, 70.49%, 70.14%, 70.36%; theoretical for In_2S_3, 70.48%. Spectrographic analysis of the precipitated sulfide showed it to be free of all but traces of impurities.

An attempt was made to prepare fairly large amounts of In_2S_3 by heating indium shot with excess sulfur in a sealed evacuated Pyrex tube. Although heating was controlled carefully and the temperature raised very slowly, the heat of reaction was so large that an explosion always resulted. Apparently, this method is satisfactory only for the preparation of small quantities, or if used for preparation of larger quantities (50–100 g.) would require specially strengthened reaction tubes of glass or other inert material.

Experimental Procedure.—Indium–sulfur mixtures of varying composition were made by melting together weighed amounts of pure In_2S_3 and In in the Vycor melting point tube, under an atmosphere of helium gas, in the induction furnace. Each mixture was melted thoroughly and held above the melting point with shaking for 10–15 minutes to assure complete reaction and mixing before the cooling curve was run. Temperature readings were taken every ten seconds. The melt was agitated during cooling to prevent supercooling, both hand shaking and mechanical vibration being used. A total of 77 such cooling curves were run on different In–In_2S_3 mixtures. Temperature was plotted against time to obtain the cooling curves.

As an aid to interpretation of the cooling curves, portions of the cooled melt in each case were polished and etched as

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[1] Presented at the XIIth International Congress of Pure and Applied Chemistry at New York City, September, 1951.

[2] A. Thiel and H. Luckmann, *Z. anorg. allgem. Chem.*, **172**, 353 (1928).

[3] T. Moeller, THIS JOURNAL, **63**, 2626 (1941).