sible abnormalities in the high pressure, low temperature part of the critical curves but experimental difficulties precluded an investigation of this region.

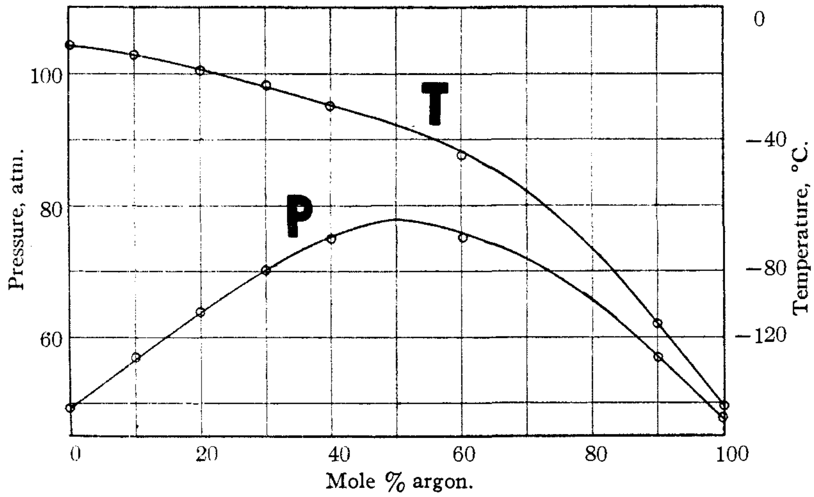

Fig. 9.—Maximum temperature of liquefaction and corresponding pressure.

Summary

The critical phenomena of the system boron trifluoride–argon exhibited the usual retrograde condensation and a new phenomenon best described as retrograde immiscibility at the low temperature, high pressure range.

The compounds formed by the gases at their melting point are practically completely dissociated at the "critical temperature region" which is about 100° higher, and so affect the curve of the maximum temperature of liquefaction only very slightly.

CLEVELAND, OHIO

RECEIVED JUNE 19, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Temperature Coefficients in the Acid Hydration of Sodium Pyrophosphate

BY SAMUEL J. KIEHL AND EDWARD CLAUSSEN, JR.

Introduction

Normal sodium pyrophosphate in aqueous or alkaline solution on long standing at room temperature or even at the boiling point does not change to orthophosphate.[1,2] In acid solution, however, this change takes place, and its rate is dependent upon the concentration both of pyrophosphate and of the acid, used as the so-called catalyst, and the temperature.[3] The rate of change to the orthophosphate in the presence of hydrochloric acid has been measured at 45°,[3] and under very special conditions at 20 and 40° by Muus,[4] who also mentioned work at 100° although no data were presented. In general data at higher temperatures are meager.[5]

In the literature many procedures for measuring the rate of this and similar reactions are published, among which have been methods based upon gravimetric analysis, change of concentration of hydrogen ions, conductivity, colorimetry, nephelometry and volumetric analysis. For purposes of this investigation, however, a modification of the method devised earlier[2] was found to be most convenient. The unchanged pyrophosphate was determined gravimetrically in the presence of orthophosphate which was formed and the velocities at 30, 45, 60, 75 and 90° were secured. From data thus obtained temperature coefficients at fifteen-degree intervals were determined.

Preparation of Materials and Apparatus

The normal sodium pyrophosphate, the disodium orthophosphate and the hydrochloric acid were prepared as described previously.[3]

In the preparation of the zinc acetate reagent used in the analysis both the zinc acetate and the acetic acid were carefully purified to eliminate possible traces of heavy metals—especially iron and lead whose pyrophosphates would interfere in subsequent operations. The final solution of the zinc acetate reagent contained a 0.2 molar zinc acetate with sufficient acetic acid to give a *p*H value of 3.3.

A magnesia mixture without ammonia was prepared by dissolving 50 g. of $MgCl_2 \cdot 6H_2O$, 100 g. of NH_4Cl, and 5 cc. of 13 *M* HCl in one liter of water.

---

(1) Rose, *Ann.*, **76**, 2 (1850).

(2) Kiehl and Coats, THIS JOURNAL, **49**, 2180 (1927).

(3) Kiehl and Hansen, *ibid.*, **48**, 2802 (1926).

(4) Muus, *Z. physik. Chem.*, **A159**, (4) 268 (1932).

(5) Abbott, THIS JOURNAL, **31**, 763 (1909), studied the conversion of pyrophosphoric acid itself at 75 and 100°.

Water-baths at 30, 45, 60 and 75° and an oil-bath at 90° all of which were controlled by Beaver[6] regulators were used to maintain the required temperatures. The maximum deviation was ±0.02°.

Bottles of 750-cc. capacity made of acid and alkali resisting glass (trade name "No Solvit") were used to contain solutions in the baths at all temperatures except 90°. For 90° it was necessary, for the prevention of losses due to evaporation, to use a specially designed Pyrex (a borosilicate glass) glass bottle from which samples could be withdrawn through a capillary tube provided with a stopcock.

Method of Analysis

Determination of Pyrophosphates in the Presence of Orthophosphate.—The method of separation of pyrophosphate from orthophosphate and the subsequent determination of pyrophosphate was developed and conditions were established by the analysis of solutions of known mixtures whose respective phosphate content and conditions would correspond to those found in course of the actual hydration in the various solutions. The separations were made in a solution whose volume was 75 cc. and whose *p*H value of 3.3 to 3.5 was obtained by the addition of three molar acetic acid and the required amount of distilled water. The standard for *p*H value was brom phenol blue with the "Wulff" series of color standards. During the precipitation in the development of the method it was found that a slow formation of the zinc pyrophosphate was essential for the formation of a crystalline precipitate and for results of separation and analysis which would meet the required precision. This was accomplished by a dropwise addition of 10 to 30% excess of the reagent with constant and uniform stirring. The precipitate was separated from the supernatant liquid and was washed till free from the excess precipitant by repeated centrifuging and decanting through the filter and was transferred to the filter. The precipitate on the filter was ignited in platinum with the usual precautions, from gentle heating at first over a bunsen flame to constant weight finally over a meker burner. In the preliminary experimentation it was found that reprecipitations were unnecessary if manipulations were carefully and accurately done.

As a further confirmation of the method of separation and analysis the orthophosphate in the filtrate from the zinc pyrophosphate was also determined in known mixtures and some examples of the subsequent hydrations by the modified magnesia mixture method of Epperson[7] the data and results for which are to be found elsewhere.[8]

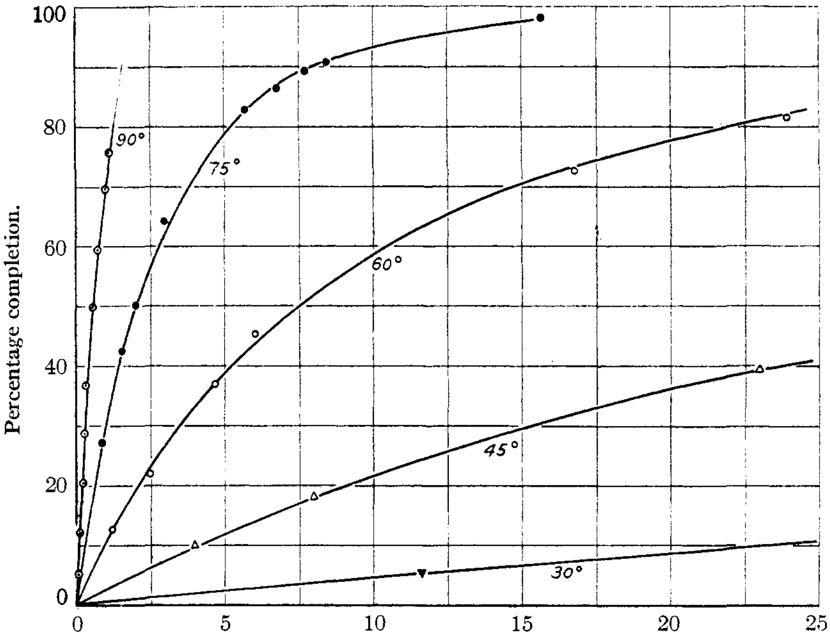

Fig. 1.—Effect of temperature on velocity.

Experimental

At each of five temperatures, 30, 45, 60, 75 and 90°, the velocity of conversion was measured for 0.125 *M* sodium pyrophosphate in the presence of 0.500 *M* (A), 0.425 *M* (B) and 0.350 *M* (C) hydrochloric acid, respectively.

Convenient samples were withdrawn by pipet, cooled quickly to room temperature, and weighed out in Bailey burets. The volume and hence the total weight of phosphorus was calculated from the known densities. The solution was then made just alkaline with concentrated ammonium hydroxide, and analyzed for the amount of phosphorus as pyrophosphate.

More detailed data for this work at all temperatures are available elsewhere.[8]

In Fig. 1 the effect of the five different temperatures upon the velocity of the reaction is shown for the solution designated A. The solutions styled B and C give the same type of curves.

Figure 2 shows the effect of the three different initial acid concentrations for the solutions at 45°.

In Table I a complete summary of these two effects upon the velocity is given for convenient equally spaced percentages of completion. The data were obtained from the curves for the hydrations in the respective solutions.

---

(6) Beaver and Beaver, *Ind. Eng. Chem.*, **15**, 359 (1923).

(7) Epperson, THIS JOURNAL, **50**, 321 (1928).

(8) E. Claussen, Jr., Dissertation, Columbia University, 1934.

TABLE I

EFFECT OF TEMPERATURE ON VELOCITY

Concentration of $Na_4P_2O_7$ = 0.125 *M*

Percentage hydrated	Time in hours for given temperatures, °C. 30	45	60	75	90
	Solution A; HCl, 0.500 *M*				
10	24.0	4.0	0.8	0.4	0.10
20	48.0	10.0	2.2	.6	.13
30	76.8	17.0	3.6	1.0	.30
40	120.0	25.0	5.2	1.5	.50
50	178.0	35.0	7.3	2.0	.60
60	261.6	47.0	10.5	2.5	.80
70	384.0	67.0	15.0	3.6	1.00
80	528.0	100.0	22.4	5.2	1.40
90	948.0	155.0	36.7	8.4	
	Solution B; HCl, 0.425 *M*				
10	45.6	6.0	1.8	0.55	0.16
20	96.0	15.0	3.7	1.05	.29
30	168.0	29.0	6.1	1.60	.45
40	271.2	47.0	9.0	2.30	.62
50	400.8	70.0	13.8	3.30	.83
60	578.4	96.0	20.1	4.50	1.10
70	873.6	146.0	28.4	6.20	1.41
80	1344.0	217.0	40.8	8.70	2.00
90	2184.0	355.0	66.0	12.80	
	Solution C; HCl, 0.350 *M*				
10	120.0	19.0	3.8	0.9	0.17
20	268.8	44.0	7.5	1.7	.37
30	468.0	74.0	11.9	2.7	.63
40	756.0	114.0	17.8	3.9	.90
50	1159.2	168.0	25.7	5.4	1.23
60	1728.0	241.0	36.7	7.2	1.60
70	2496.0	342.0	52.0	9.7	2.08
80	3504.0	489.0	80.0	13.7	2.96
90			122.0	21.4	

Discussion and Determination of Temperature Coefficients.—In order that temperature coefficients may be obtained for the reaction under the chosen experimental conditions, an equation will be necessary which will embody a factor that may be employed in establishing a unit of measure for the effect of temperature only upon the rate. This factor should remain constant under the prescribed conditions upon a definite temperature level but its value should change in going from one temperature level to another if it is to be of service for the determination of temperature coefficients. If the reaction under the conditions conformed to one of the classical orders of reaction in which the velocity constants incorporate this factor in the mathematical expression of the reaction which changes with temperature the problem would be simple. But the rate is affected greatly by a variation of the concentration of hydrogen ions[3] which on account of the difference in activity of the pyrophosphoric and orthophosphoric acids undergoes a marked decrease as the reaction proceeds. This decrease is dependent jointly upon the initial concentration of the hydrochloric acid and of the pyrophosphate.[3]

Moreover, for the proportions in which the original acid and pyrophosphate are used, the decrease of concentration of hydrogen ions during the reaction is sufficient to effect a considerable variation in the velocity. The difference in the speeds for A and B is greater at 90% completion than earlier, as reference to the slopes of the curves in Fig. 2 will show.

Therefore, due to the difference in activities of the respective phosphoric acids which causes changes in the concentration of hydrogen ions, it has been found that the reaction under discussion cannot be expressed by any of the orders of reaction unless the concentration of hydrogen ion be made to remain constant or a mathematical relation be obtained whereby it may be expressed in terms of the concentration of the phosphate.

This conclusion is supported by the work of Abbott[5] and by the work of Kiehl and Hansen.[3]

In more recent work by Muus,[4] who used radically different experimental conditions and approximately constant ionic environment at 20 and 40°, it was shown that with an extreme excess of acid (from 38 to 150 times the concentration of pyrophosphate), and in the presence of constant kinetic conditions (about 1000 times as much potassium chloride as the initial concentration of pyrophosphate), a definitely constant first order reaction velocity constant was obtained with a given concentration of hydrogen ion. These constants were directly proportional to the various concentrations of hydrogen ion under which the reaction was studied.

Consequently in this work, where the order of magnitude of the initial concentration of hydrogen ion was the same as that of the pyrophosphate, and where the inevitable consequence was that the concentration of hydrogen ion varied throughout the reaction recourse to an empirical equation to express the reaction rate seemed to be the only resort. The form of the equation was tentatively established by data from solutions at 45°[3] where concentrations of both hydrogen ion and pyrophosphate were known. Since the pyrophosphate concentration was the same in all solutions at the beginning and the initial concentration of hydrochloric acid was fixed for solution C, it was possible to express the concentration of hydrogen ion in terms of the pyrophosphate remaining, (x). By using such respective values from actual measurement made in synthetic solution at convenient percentage intervals, an equation of the form $(H^+) = A' + B'x + C'x^2 + D'x^3 + \ldots$, may be developed to express the relationship. The constants A', B', C', D', etc., may then be evaluated by solution of simultaneous equations. The velocity of the reaction accordingly may be expressed in the general equation $dx/dt = kf[x(H^+)]$, which by substitution of the above equation for $[H^+]$, assumes the form, $dx/dt = kx(A' + B'x + C'x^2 + D'x^3 +)$. The integration of this expression gives the final equation

$$kt = A \log x + B + Cx + Dx^2 \ldots$$

with t as time, x the fraction of the concentration of the pyrophosphate remaining, and k, A, B, C, D constants. The constants were evaluated by solving simultaneous equations representing times at 25, 35, 45, 55, 65 and 75% completion which were determined from a large smoothed-out plot of percentage against time for solution A at 60°.

Thus solved, the completed equation is

$$kt = -102.860 \log x - 68.143 + 109.690x - 42.598x^2 \ldots$$

It is noteworthy that although the equation was developed from data for solution A at 60° (0.125 M pyrophosphate and 0.500 M hydrochloric acid), it, with reasonable dependability, expresses the behavior not only of solutions A at all temperatures but also of solutions B and C throughout the entire temperature range.

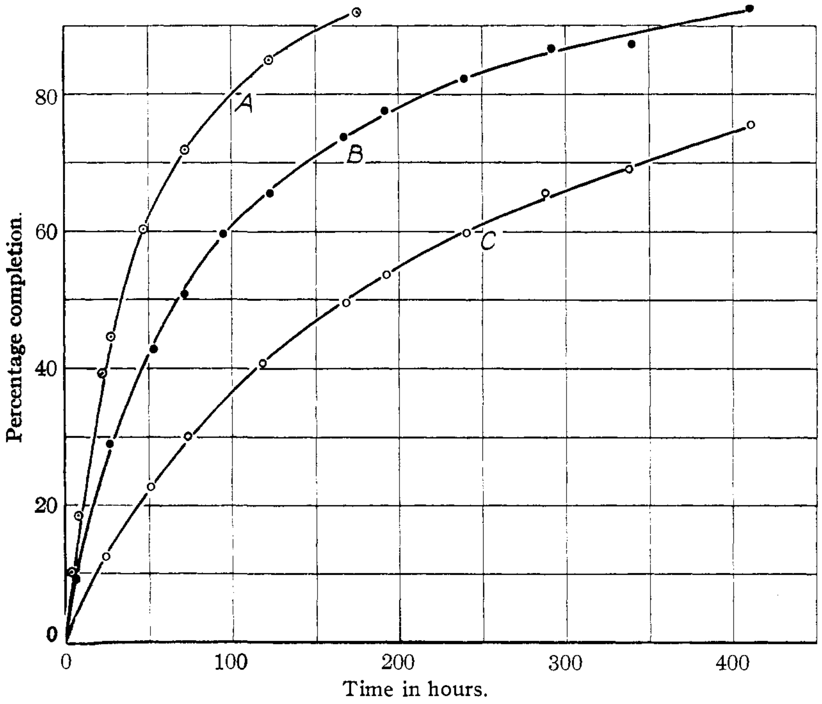

Fig. 2.—45° data—effect of initial acid concentration on velocity.

By the use of this equation with all data within the limits of 25 to 75% completion, Table II was compiled. The values in Column 5 (% a. d.) were calculated from the ratio of the average deviation from the mean values of K.

The comparative constancy indicated by the average deviation of the calculated reaction velocity constants for the various solutions with the same concentration of acid at the same temperature and the consistency of change of constants for the various solutions from temperature to temperature suggest that they represent a reliable conception of the different reaction rates for the changes in initial acid concentrations and the changes in temperature. The equation holds best for the three intermediate temperatures.

TABLE II

REACTION VELOCITY CONSTANTS CALCULATED FROM THE EMPIRICAL EQUATION

Solution	T., °C.	No. calculations	Mean k	Average deviation, %
A	90	4	11.60	7.4
B	90	5	8.74	5.7
C	90	3	5.75	1.0
A	75	4	3.64	2.7
B	75	4	2.17	2.3
C	75	3	1.30	2.7
A	60	3	0.966	0.3
B	60	4	.502	1.9
C	60	4	.276	2.0
A	45	4	.215	1.9
B	45	5	.102	2.3
C	45	6	.0425	3.0
A	30	4	.0393	2.6
B	30	8	.0180	6.3
C	30	7	.00626	7.5

By plotting these reaction velocity constants against temperature (Fig. 3) the customary exponential type of curve is obtained for each of the three solutions.

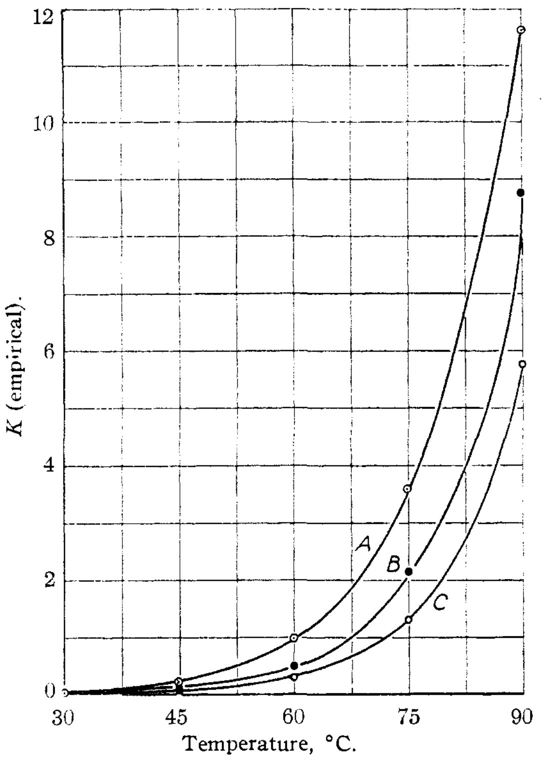

Fig. 3.—Effect of temperature on reaction velocity constant.

Temperature Coefficients

In Table III temperature coefficients calculated from the mean reaction velocity constants obtained by use of the empirical equation are compared with similar coefficients obtained by dividing the time obtained from smoothed-out curves for convenient percentages, such as 40, 50, 60, 70, at one temperature with a similar reading fifteen degrees higher.

The coefficients obtained by each of the methods described are quite comparable. Both decrease

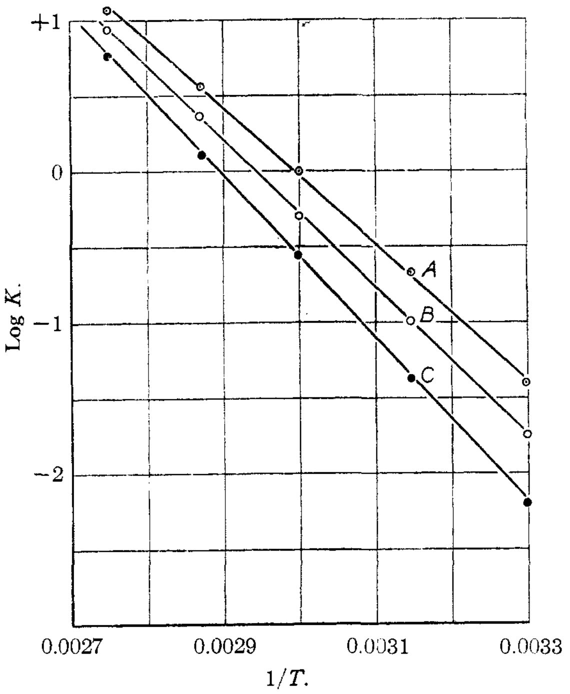

Fig. 4.—Plot of log K (empirical) *versus* the reciprocal of the absolute temperature.

TABLE III

TEMPERATURE COEFFICIENTS

Solution			45/30°	60/45°	75/60°	90/75°
	From mean value of K		5.47	4.63	3.65	3.19
A	From time data	40% completion	4.8	4.8	3.5	3.1
		50% completion	5.0	4.8	3.7	3.4
		60% completion	5.6	4.5	4.2	3.3
		70% completion	5.7	4.5	4.2	3.6
	Mean		5.3	4.7	3.9	3.4
	From mean value of K		5.67	4.92	4.32	4.03
B	From time data	40% completion	5.8	5.2	3.9	3.7
		50% completion	5.7	5.1	4.2	4.0
		60% completion	6.0	4.8	4.5	4.1
		70% completion	6.0	5.1	4.6	4.3
	Mean		5.9	5.1	4.3	4.0
	From mean value of K		6.79	6.49	4.71	4.42
C	From time data	40% completion	6.6	6.4	4.7	4.2
		50% completion	6.9	6.5	4.9	4.3
		60% completion	7.2	6.6	5.1	4.5
		70% completion	7.3	6.6	5.4	4.7
	Mean		7.0	6.5	5.0	4.4

rather regularly with increase of initial concentration of hydrochloric acid at all temperatures, as we pass from solution C to B to A. Since the activity of the acid is greater at the beginning than at the end of the reaction the individual coefficients from the time method in any given solution tend to be greater as the reaction proceeds. Consequently the mean coefficients decrease as the temperature is raised.

If the reaction velocity constants which have been determined by use of the empirical equation be plotted, log K against $1/T$ (Fig. 4), in conformance with the differential form of the Arrhenius equation, $\mathrm{d}\ln k/\mathrm{d}T = Q/RT^2$, a straight line is obtained for each of the solutions.

Moreover, from the integral form of this same equation

$$\ln \frac{k_1}{k_2} = \frac{Q}{R}\,\frac{T_1 - T_2}{T_1T_2}$$

values for Q at fifteen degree intervals may be calculated. The values thus obtained are within the usual limits of constancy.

Summary

1. New data are presented for the velocity of conversion of pyrophosphate to orthophosphate in aqueous solution in the presence of three different concentrations of hydrochloric acid at five temperatures, 30, 45, 60, 75 and 90°. $Na_4P_2O_7 \cdot 10H_2O$ was used.

2. An empirical equation for the velocity of the reaction has been developed.

3. Temperature coefficients for 15° intervals have been calculated.

4. The values for Q in the equation of Arrhenius are within the usual limits of constancy.

5. A modification of the method for the quantitative determination of pyrophosphate in presence of orthophosphate by use of zinc acetate has been made.

NEW YORK, N. Y. RECEIVED AUGUST 3, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Relative Strengths of Acids in n-Butyl Alcohol[1]

BY LELAND A. WOOTEN AND LOUIS P. HAMMETT

We have measured the relative strengths of a series of substituted carboxylic and phenolic acids in n-butyl alcohol, a hydroxylic solvent of relatively low dielectric constant, and have found certain relationships between the structure of the acid and the effect upon the relative strength of the transfer of the acid from water to this solvent. The solubility of lithium chloride in this solvent made it possible to work in a medium of high and constant strength, a necessary condition for the measurement of relative acid strength by the potentiometric method if specific salt effects are to be minimized or eliminated and the uncertainty due to liquid junction potentials avoided. Butylate ion was employed as the base.

Experimental

Method.—Concentration cells of the following type were set up and measured

$$\begin{array}{c|c||c||c|c} & \frac{\mathrm{HA_1}}{\mathrm{NaA_1}} = 1 & & \frac{\mathrm{HA_2}}{\mathrm{NaA_2}} = 1 & \\ \mathrm{Au} & & \text{Satd. soln.} & & \mathrm{Au} \\ & \mathrm{LiCl},\ 0.05\ M & \text{of LiCl} & \mathrm{LiCl},\ 0.05\ M & \\ & \text{Quinhydrone} & & \text{Quinhydrone} & \\ \multicolumn{2}{r}{\text{a}} & & \multicolumn{2}{l}{\text{b}} \end{array}$$

The electromotive force of this cell at 25° is related to the relative strength of the two acids, HA_1 and HA_2, by the expression

$$\text{E. m. f.}/0.0591 = pK_2 - pK_1 = \Delta pK$$

where $pK = -\log K$, the negative logarithm of the ionization constant of the acid. This expression is a sufficiently precise approximation provided the acids exhibit normal weak-acid titration curves in the solvent under study. Since a fairly high neutral salt concentration (LiCl) was maintained throughout the whole system the junction potentials at a and b should be small and practically constant.

The cell used was essentially that employed by Hammett and Dietz.[2] Mixing of the solutions was minimized by ground glass plugs, which separated the buffer solutions from the salt bridge. The buffer solutions were approximately 0.0025 M and in all cases were made 0.05 M with respect

---

[1] Dissertation submitted by Leland A. Wooten to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, April, 1935. The material was presented at the New York meeting of the American Chemical Society, April, 1935.

[2] Hammett and Dietz, THIS JOURNAL, **52**, 4795 (1930).