pair they form has three degrees each of translational and rotational freedom. By insisting on contact in pairs, vibrational freedom is excluded.

It is of interest to compare (22) with the value K^{-1} derived from the Bjerrum–Fuoss function. The latter has been used mostly in the range of large b values, where the asymptotic expansion[11] may be used

$$K^{-1} = (4\pi La^3/1000)(e^b/b) \qquad (23)$$

When b is substantially larger than two, the exponential function e^b almost completely masks the b in the denominator, and over a considerable range e^b and (e^b/b) can approximate each other, with slightly different a-values. There is a slight systematic trend visible in the a-values reported by Fuoss and Kraus[11] for tetra-isoamylammonium nitrate in dioxane–water mixtures, but the average value of 6.40 Å. so well reproduced the data over a range of 10^{15} in K-values that the trend was ignored. Now, of course, we feel that it is real and is a consequence of the unnecessary b in the denominator of the function (23). Denison and Ramsey[2] in fact showed that the early data conform well to the simpler function which they proposed. When b is less than 4 or 5, the difference between e^b and e^b/b is, of course, easy to see, but data in this range of dielectric constants failed to reveal the inadequacy of the Bjerrum function, because the K-values calculated by conventional means from the data were forced to absorb the then unknown linear and c log c terms from electrophoresis and relaxation. Consequently, when $\mathring{a}$-values were calculated from the experimental K-values by means of the Bjerrum function for the systems in nitrobenzene mixtures, for example, and were found to vary systematically with dielectric constant, the discrepancy was ascribed to the missing higher terms rather than to the function itself.[12] In other words, when the K-values were reliable, the presence or absence of b in the denominator was not detectable, while in the range where the two functions are visibly different, the K-values were not considered suitable for comparison with theory. Based on information now available, an equation of the form of (22) rather than that of (23) should be used in future treatment of ion pairs. Incidentally, a similar revision of the theory of association to ion triples[13,14] and quadrupoles[15] will also have to be made.

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[11] R. M. Fuoss and C. A. Kraus, This Journal, **55**, 1019 (1933); equation 7.

[12] H. Sadek and R. M. Fuoss, *ibid.*, **72**, 301 (1950); **76**, 5897, 5902, 5905 (1954).

[13] R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 2387 (1933).

[14] R. M. Fuoss, *ibid.*, **56**, 1857 (1934).

[15] R. M. Fuoss and C. A. Kraus, *ibid.*, **57**, 1 (1935).

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Acid–Base Reactions in Fused Salts. I. The Dichromate–Nitrate Reaction

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The reaction $2Cr_2O_7^{=} + 4NO_3^{-} \rightarrow 4NO_2 + O_2 + 4CrO_4^{=}$ proceeds at a measurable rate in fused KNO_3–$NaNO_3$ eutectic at 250°. A kinetic study of the reaction demonstates that the mechanism consists of two steps: the equilibrium $Cr_2O_7^{=} + 2NO_3^{-} \rightleftarrows N_2O_5 + 2CrO_4^{=}$ followed by the slow step $N_2O_5 \rightarrow$ decomposition products. The presence of the equilibrium is demonstrated by adding metal ions which precipitate the chromate and noting the effect on the reaction rate. Also, one of the metal ions, Pb^{++}, is known to form complex ions with Cl^{-}; the effect on the rate of adding Pb^{++} and Cl^{-} simultaneously also shows the presence of the equilibrium reaction.

Equilibrium studies have been made of a number of Lewis acid–base systems in fused salts.[1] However, no acid–base systems have been studied in which the equilibrium constant is very small; one technique for detecting an equilibrium which lies very much to the left is to study kinetically a reaction of one of the equilibrium products. The reaction between dichromate and nitrate in fused KNO_3–$NaNO_3$ eutectic produces very little of the equilibrium acidic product and chromate: $Cr_2O_7^{=} + 2\ NO_3^{-} \rightleftarrows N_2O_5 + 2CrO_4^{=}$. The decomposition of the acidic product is susceptible to kinetic study, however, and the presence of the equilibrium may be shown by studying the effect of variation in concentration of the stable equilibrium product, chromate; this is accomplished by adding various metal nitrates in varying concentration which precipitate the chromate ion.

Experimental

Materials and Apparatus.—ACS reagent grade chemicals were used. All of the rate determinations were carried out in test-tube-shaped Pyrex reaction vessels immersed in a constant temperature bath consisting of a fused mixture of alkali nitrates. The temperature was maintained to within ±1° with a chromel–alumel indicating thermocouple controlling a Brown Potentiometer Pyrometer.

The reaction vessel used for most of the experiments was made from 31 mm. i.d. Pyrex tubing. A 40/50 standard taper glass joint at the top was used to give easy access to the solution and was fitted with a gas inlet tube which reached to within one-half inch of the bottom of the reaction vessel, and an outlet tube extending from the cap. This arrangement allowed one to agitate the reacting solution and to sweep any gaseous products out and into the absorbing solutions with a sweep gas.

The sweep gas (from cylinders) was first dried by passing it through a U tube containing anhydrous $Mg(ClO_4)_2$ and then preheated in coiled glass tubing immersed in the fused salt bath. The flow rate of the gas through the solution was determined with a gas flowmeter.

Procedure.—A solution of the precipitant ion in the fused eutectic was added to a dichromate solution in the same solvent. A total of 100 g. of solvent was used in each run. The solutions were maintained at the bath temperature.

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[1] H. Flood and T. Forland, *Acta Chem. Scand.*, **1**, 592, 781 (1947); H. Flood, T. Forland and B. Roald, *ibid.*, **1**, 790 (1947); H. Flood and A. Muan, *ibid.*, **4**, 364 (1950).

A fine precipitate usually formed immediately but settled sufficiently in a few minutes so that samples essentially free of suspended precipitate could be withdrawn without filtering.

The rate of the precipitation of the chromate salt was studied by following the change in the dichromate concentration with time. Samples weighing approximately one gram were withdrawn with a preheated pipet and analyzed for dichromate content, using an iodine–thiosulfate titration. Zero time of the reaction was taken as the time of withdrawal of the first sample.

In experiments using a sweep gas to stir the solution, the time during which the flow of the sweep gas was stopped in order to allow the precipitate to settle and to withdraw samples was small enough (less than 5 minutes) relative to the time between samples that the effect on the rate could be neglected in most cases.

The acid content of the gases produced during the reaction was determined by absorption in standard alkali.

Results and Discussion

In the absence of a precipitant for chromate, solutions of dichromate in fused KNO_3–$NaNO_3$ eutectic are stable for long periods of time; thus, all of the experiments were done with a precipitant for chromate in the reaction mixture. Early in the study it was found that the flow rate of sweep gas affected the rate of formation of chromate. The order in dichromate was found to be one, independent of the flow of gas through the mixture. The effect of the flow rate of sweep gas is shown in Table I. It was found that very reproducible results could be obtained with a flow rate of sweep gas of 0.21 l. per min. and, under these circumstances, the $[Cr_2O_7^{=}]$ and the acidic gases produced could be measured as a function of time. Since the vessel was opened for sampling from time to time, the kinetic data were taken from the dichromate analyses.

TABLE I

VARIATION OF PSEUDO FIRST-ORDER RATE CONSTANT WITH QUANTITY OF SOLUTION AND FLOW RATE OF THE SWEEP GAS THROUGH THE SOLUTION

Nitrogen sweep gas, $[Pb^{++}] = 0.044$ *m*, initial $[Cr_2O_7^{=}] =$ 0.0030 to 0.0070 *m*.

Total solvent, g.	$k' \times 10^5$ (sec.$^{-1}$) Nitrogen flow rate (l. per min.) 0	0.21	0.73.	170
45	2.6	3.9	6.0	8.1
95	2.1	3.4	4.9	6.9
195	1.67	..	3.8	..

The effect of the sweep gas on the reaction rate suggested an equilibrium involving a gaseous product

$$2M^{++} + Cr_2O_7^{=} + 2NO_3^{-} \rightleftarrows N_2O_5\ (\text{soln.}) + 2MCrO_4 \quad (1)$$

The rate-controlling step then, would be the rate of removal of N_2O_5 either by volatilization or decomposition in solution

$$N_2O_5 \longrightarrow N_2O_5\ (\text{gas})$$

$$N_2O_5 \longrightarrow \text{decomposition products} \quad (2)$$

The rate expression is

$$-\frac{d[Cr_2O_7^{=}]}{dt} = k[N_2O_5] \quad (3)$$

providing the decomposition reaction is first order n N_2O_5; the experimental first order found for dichromate fixes the over-all order in N_2O_5 as unity

$$K_1 = \frac{[N_2O_5][CrO_4^{=}]^2}{[Cr_2O_7^{=}]} \quad (4)$$

$$-\frac{d[Cr_2O_7^{=}]}{dt} = \frac{kK_1[Cr_2O_7^{=}]}{[CrO_4^{=}]^2} \quad (5)$$

Combination of equation 5 with the solubility product constant for the metal chromate yields

$$-\frac{d[Cr_2O_7^{=}]}{dt} = \frac{kK_1[Cr_2O_7^{=}][M^{++}]^2}{K_{sp}^2} \quad (6)$$

where $K_{sp} = [M^{++}]\ [CrO_4^{=}]$. The experimental order in $[M^{++}]$ should be two, and this value is found when M^{++} is Ba^{++} or Ca^{++}. When M^{++} is Pb^{++}, however, the order in lead ion varies between one and two, decreasing as $[Pb^{++}]$ increases. This is shown in Table II. The variable order in $[Pb^{++}]$ suggests another equilibrium

$$Pb^{++} + Cr_2O_7^{=} \rightleftarrows PbCr_2O_7$$

and

$$K_2 = \frac{[PbCr_2O_7]}{[Pb^{++}][Cr_2O_7^{=}]} \quad (7)$$

TABLE II

VARIATION OF PSEUDO FIRST-ORDER RATE CONSTANT WITH LEAD ION CONCENTRATION

Initial $[Cr_2O_7^{=}] = 0.0030$ to 0.0040 *m* N_2 flow rate = 0.21 l. per min., 95 g. of solvent.

250° $[Pb^{++}]$, *m*	$k' \times 10^5$	300° $[Pb^{++}]$, *m*	$k' \times 10^5$
0.044	3.0 ± 0.2	0.012	0.48
0.094	8.8 ± 0.4	.021	1.10
		.023	1.4
		.044	3.4 ± 0.2
		.094	8.9 ± 0.3
		.194	17.7 ± 1.0

Total dichromate, $T_{Cr_2O_7^{=}}$, then is divided between $[PbCr_2O_7]$ and $[Cr_2O_7^{=}]$. Thus

$$K_2 = \frac{T_{Cr_2O_7^{=}} - [Cr_2O_7^{=}]}{[Pb^{++}][Cr_2O_7^{=}]}$$

and

$$[Cr_2O_7^{=}] = \frac{T_{Cr_2O_7}}{K_2\ [Pb^{++}] + 1} \quad (8)$$

If the $[Pb^{++}]$ is much greater than $T_{Cr_2O_7^{=}}$, one may consider total lead ion equivalent to $[Pb^{++}]$. A combination of equations 6 and 8 yields

$$\frac{dT_{Cr_2O_7^{=}}}{dt} = \frac{kK_1[Pb^{++}]^2T_{Cr_2O_7^{=}}}{(K_2[Pb^{++}] + 1)K_{sp}^2} \quad (9)$$

The chemical method of analysis used determines $T_{Cr_2O_7^{=}}$ as a function of time. Equation 9 may be seen to be in the form of a first-order equation at high Pb^{++} concentrations, with

$$k' = \frac{kK_1[Pb^{++}]^2}{(K_2[Pb^{++}] + 1)K_{sp}^2}$$

The pseudo-constants, k', are evaluated from the slopes log $T_{Cr_2O_7^{=}}$ *vs.* time plots at various Pb^{++} concentrations. It will be noted that

$$1/k' = \frac{K_{sp}^2K_2}{kK_1[Pb^{++}]} + \frac{K_{sp}^2}{kK_1[Pb^{++}]^2}$$

Experimental values for $1/k'$ at various $[Pb^{++}]$ are taken from the data in Table II. Figure 1 is a plot of $[Pb^{++}]/k'$ *vs.* $1/[Pb^{++}]$. It is evident that the intercept divided by the slope is K_2. The value taken from the graph for K_2 is 45 ± 5.

The product of the constants, kK_1, may be obtained from the slope of the plot in Fig. 1, provided K_{sp} is known; these solubility product constants were determined for $PbCrO_4$, $CaCrO_4$ and $BaCrO_4$ by direct solubility measurements.[2] Table III shows a comparison of K_{sp} as determined kinetically and from solubility for the $BaCrO_4$ and $CaCrO_4$ salts; the value for kK_1 was taken from the results where Pb^{++} was used as precipitant for chromate. The lack of agreement in the case of $CaCrO_4$ is believed to be caused by a tendency for $CaCrO_4$ to supersaturate, that is, $CaCrO_4$ may precipitate slowly relative to the rate of formation of the chromate ion.

TABLE III

COMPARISON OF SOLUBILITY PRODUCTS OF CHROMATES OBTAINED FROM KINETIC DATA AND DIRECT CHEMICAL MEASUREMENT

Chromate salt	Solubility product (K_{sp}) Kinetic data[a]	Chemical measurement[b]
$BaCrO_4$ (two expt.)	6.3×10^{-6}	4.0×10^{-6}
	4.7×10^{-6}	
$CaCrO_4$	0.12×10^{-4}	1.7×10^{-4}

[a] Solubility product calculated from the equation

$$K_{sp} = \frac{k'_{Pb}K^2_{sp}(Pb)(M^{++})^2[1 + 47(Pb^{++})]^{1/2}}{k_M'(Pb^{++})^2}$$

where k' = pseudo first-order rate constant for the metal indicated by subscript, K_{sp} = solubility product and M^{++} = barium or calcium. [b] Direct chemical measurement by analysis of chromate concentration in a saturated $CaCrO_4$ solution.

The Effect of Chloride Ion.—As a further test of the equilibrium in equation 1, chloride ion was added along with lead ion in a number of runs. The association constants of Pb^{++} with Cl^- have been determined,[1] and by use of the equation

$$Pb^{++}_{total} = [Pb^{++}] + [PbCl^+] + [PbCl_2] + [PbCl_3^-]$$

combined with the equilibrium expressions for the formation of the complex ions, one may show that

$$[Pb^{++}] = \frac{Pb^{++}_{total}}{1 + B_1[Cl^-] + B_2[Cl^-]^2 + B_3[Cl^-]^3} \quad (10)$$

The values of the B's, where

$$B_n = \frac{[PbCl_n{}^{2-n}]}{[Pb^{++}][Cl^-]_n}$$

are 6, 17 and 17 for B_1, B_2 and B_3, respectively (concentrations in molalities) at 300°.[2] The concentration of dichromate was too low in these experiments for a significant fraction of the $[Pb^{++}]$ to be in the form of $PbCr_2O_7$. Table IV shows the $[Pb^{++}]$ calculated from equation 10 compared with that determined kinetically.

The two results agree well, since the constants B_2 and B_3 are known only approximately, and any sluggishness in the attainment of equilibrium between Pb^{++} and Cl^- would show a too high lead ion concentration from the kinetic data.

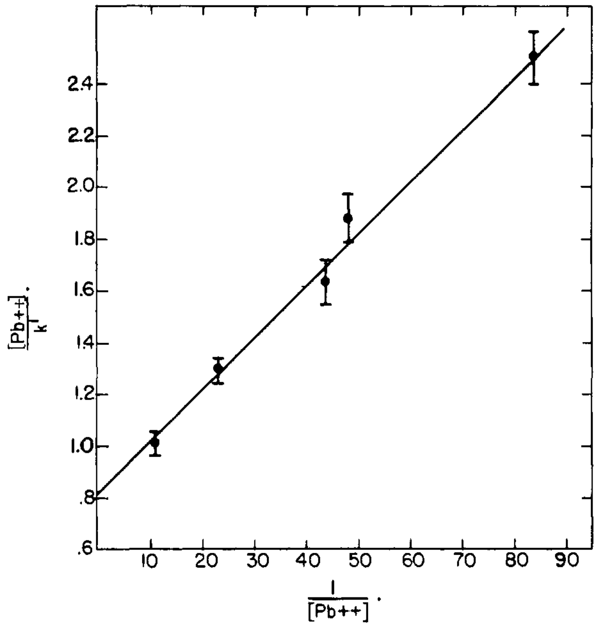

Fig. 1.—Plot of reciprocal of equation 9 to evaluate K_2.

TABLE IV

COMPARISON OF LEAD ION CONCENTRATION IN SOLUTIONS CONTAINING CHLORIDE CALCULATED FROM SOLUBILITY DATA AND KINETIC DATA

300°, initial $[Cr_2O_7^{=}]$ = 0.0050 *m*, 95 g. of solvent, N_2 flow rate = 0.21 l./min.

KCl	$k' \times 10^5$, sec.$^{-1}$	Pb^{++}_{total}, *m*	$[Pb^{++}]$, *m* Solubility data	Kinetic data
0.00	3.60	0.046	0.046	0.046
.25	0.91	.048	.016	.018
.50	.31	.048	.007	.0094
.75	.18	.048	.003	.0070
1.00	.043	.048	.0013	.0030

The Nature of the Acidic Equilibrium Product.—In the discussion thus far, the acidic equilibrium product has been written as N_2O_5. The probability is good that the N_2O_5 is highly dissociated in the alkali nitrate solvent

$$N_2O_5 \rightleftarrows NO_2^+ + NO_3^-$$

The fact that the sweep gas removes the product suggests that some N_2O_5 is indeed present. The low rate of decomposition of the N_2O_5, however, suggests that some sort of stabilization is involved, and in this highly ionic medium it is likely that the N_2O_5 is stored as NO_2^+.

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[2] F. R. Duke and M. Iverson, *J. Phys. Chem.*, **62**, 417 (1958).