

powder is vigorously stirred under 1 liter of refluxing anhydrous ether. One mole of the alkoxybenzyl halide dissolved in 1 l. of ether is added over a two to five hour interval. The resulting Grignard reagent is then filtered through glass cotton to remove the finely divided magnesium powder, which if not removed usually reacts with

objectionable vigor during the ultimate decomposition with water or dilute acid. The yield is estimated by the usual acidimetric titration.

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COMMUNICATIONS TO THE EDITOR

CHEMICAL REACTIONS IN MOVING BOUNDARY SYSTEMS OF WEAK ELECTROLYTES

Sir:

In moving boundary systems containing partially neutralized weak acids or bases there exists the possibility of chemical reactions at the moving boundary which cause the mobility calculated from the boundary velocity and the conductivity of the leading solution to be lower than the ionic mobility.¹ This is illustrated by experiments 2 and 3 in which the indicator electrolyte is a salt of weak acid (cacodylic acid) having a higher pK than the leading weak electrolyte (acetic acid). The following reaction goes to completion

From equation (2) we see that the mobility, u , calculated from the boundary velocity in this case is the "constituent" mobility. The acetate ion mobility, u_{OAc}^{γ}

$$u = V^{\beta\gamma} \frac{1000}{F} = u_{OAc}^{\gamma} \frac{(C_{OAc}^{\gamma})}{(C_{OAc}^{\gamma} + C_{HOAc}^{\gamma})} \quad (3)$$

calculated from the constituent mobility obtained in experiments 2 and 3 by using equation (3) are -17.62×10^{-5} and -17.55×10^{-5} in agreement with the average value, -17.53×10^{-5} , obtained in experiments 1 and 4.

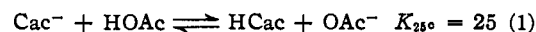
However, in systems containing weak electrolytes the constituent mobility is not always

TABLE I^a

Moving Boundary System ^b		β	α	$\frac{u \times 10^5}{(0^\circ C.)}$
γ				
(1) NaOAc(0.05)	←	NaCac	:: NaCac	-17.47
(2) NaOAc(0.05), HOAc(0.05)	←	NaCac, HCac	:: NaCac	- 8.81
(3) NaOAc(0.05), HOAc(0.01)	←	NaCac, HCac	:: NaCac	- 5.85
(4) NaOAc(0.05)	←	NaT	:: NaT	-17.59
(5) NaOAc(0.05), HOAc(0.05)	←	NaT, HOAc	:: NaT	-16.54

^a OAc, acetate; Cac, cacodylate; T, trichloroacetate. ^b The conventions recommended by Longworth, THIS JOURNAL, 67, 1109 (1945), are used.

to the right at the moving boundary so that none of the acetic acid remains behind that boundary.



The concentration of the sodium acetate is 0.05 N (at 0°) in all experiments, and it has been shown that the concentration and pH of the indicator electrolyte (α solution) is unimportant over a wide range.

The moving boundary equation² cannot be applied to acetate ion in the presence of acetic acid, but a term may be added for the acetic acid as follows so that the moving boundary equation for acetate constituent becomes

$$T_{OAc}^{\gamma} = V^{\beta\gamma} (C_{OAc}^{\gamma} + C_{HOAc}^{\gamma}) = \frac{u_{OAc}^{\gamma} C_{OAc}^{\gamma}}{\kappa \gamma 1000/F} \quad (2)^s$$

(1) Dr. Harry Svensson, Institutes of Physical and Biological Chemistry, Uppsala, Sweden, has independently recognized this fact in work initiated in September, 1946 (*Acta Chem. Scand.*, in press), personal communication.

(2) Weber, *Sitzungsber. Akad. Wissensch. Berlin*, 936 (1897); Svensson, *Ark. Kem. Min. Geol.*, 17A, No. 14 (1943); Longworth, THIS JOURNAL, 67, 1109 (1945).

(3) The symbols have the meanings used by Longworth (C_{OAc}^{γ} is taken as negative).

obtained as illustrated by experiment 5. Whether or not a chemical reaction takes place depends upon the pK and relative mobility of the indicator ion. In this experiment the mobility calculated is slightly lower than the ionic mobility because the acetate ion does not disappear in the $\beta\gamma$ boundary, owing to the slight dissociation of the acetic acid left behind the moving boundary.

Since proteins and buffers used in electrophoresis are weak electrolytes, reactions such as the above occur and must be considered in the quantitative interpretation of electrophoretic patterns.

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SYNTHESIS OF DL-THREONINE

Sir:

The structure α -amino- β -hydroxy- n -butyric acid contains two dissimilar asymmetric carbon atoms and hence exists as four optical isomers and