would not be incompatible with the solutions to be used. Thus the complete cell would be

$$\text{Tl(Hg)} \mid \text{TlClO}_4(m_1), \text{BClO}_4(m_2), \text{BOH}(m_3) \mid \text{H}_2 \quad (A)$$
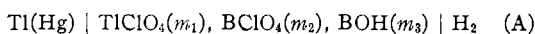
where BOH is a weak base. The potential of the cell is given by the equation

$$E = E^\circ - \frac{RT}{F}\ln\frac{[\text{Tl}^+][\text{BOH}]}{[\text{B}^+]}\,p_{\text{H}_2}^{1/2} - \frac{RT}{F}\ln K_b - \frac{RT}{F}\ln\frac{\gamma_{\text{Tl}^+}\,\gamma_{\text{BOH}}}{\gamma_{\text{B}^+}\,(\text{H}_2\text{O})} \quad (1)$$

where

$$E^\circ = E^\circ\ \text{Tl(Hg)},\ \text{Tl}^+ - E^\circ\ \text{H}_2,\ \text{H}_2\text{O},\ \text{OH}^- \quad (2)$$

K_b is the thermodynamic dissociation constant of the weak base, and the parentheses, brackets and γ's represent activities, molalities and activity coefficients, respectively. Rearranging

$$\ln K_b + \ln\frac{\gamma_{\text{Tl}^+}\,\gamma_{\text{BOH}}}{\gamma_{\text{B}^+}\,(\text{H}_2\text{O})} = \frac{E^\circ - E}{RT/F} - \ln\frac{[\text{Tl}^+][\text{BOH}]}{[\text{B}^+]}\,p_{\text{H}_2}^{1/2} \quad (3)$$

By plotting the right-hand member of this equation against the ionic strength and extrapolating to $\mu = 0$, $\ln K_b$ should be determined.

In the case of ampholytes, the situation is reversed; the electrodes of cell A serve to determine the acid dissociation constant but not the base; while the hydrogen–silver chloride cell is used to determine the base constant but not the acid.

Due to the fact that the normal potential of thallium is much lower than that of the hydrogen–hydroxide electrode, the hydrogen will reduce thallium ions unless the varying concentrations are properly adjusted. For 1 atm. pressure of hydrogen, 0.01 M Tl$^+$ and $[\text{B}^+] = [\text{BOH}]$, K_b must be less than about 10^{-6}. For stronger bases, $[\text{Tl}^+]$ and $[\text{BOH}]$ might be lowered or the partial pressure of hydrogen reduced by diluting with nitrogen, the actual pressure of hydrogen being determined by a simultaneous observation on a hydrogen–silver chloride cell using a known concentration of hydrochloric acid.

In his present situation, the writer is unable to do experimental work on cell A and is therefore describing it for the benefit of the field.

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Fluorine Preparation Cell

BY L. M. DENNIS AND E. G. ROCHOW

When the cell for the preparation of fluorine by electrolysis, described by us in THIS JOURNAL, **53,** 3263 (1931), is operated with a current of about 6 amp. (60% current efficiency), no stoppage of the side-arm D (see original figure) occurs. If, however, a current of about 10 amp. is employed (current efficiency 80%), it has been found that the electrolyte is slowly carried over into the arm D and clogs the tube. This difficulty is avoided by introducing, between D and the union E, the copper tube S (Fig. 1), and widening the tube D to one cm. internal diameter. The electrolyte that passes through D falls to the bottom of S, and by this device the continuous operation of the cell at high output over a period of several hours is made possible.
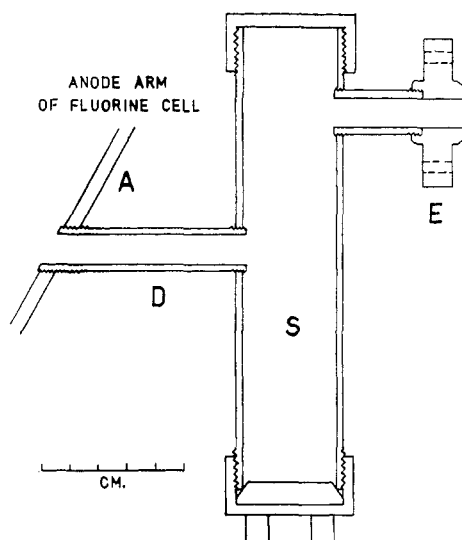

Fig. 1.

At the close of a run, the electrolyte that has collected in S falls out of the cold tube when the lower cap and conical plug are removed. If the material in S should adhere to the tube, it is easily loosened by heating the outside of the tube with the flame of a Bunsen burner.

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