Sample	*m*	ϑ
II 2	0.11674	0.21457
II 1	.13658	.24979
I 1	.14753	.26937
II 3	.16892	.30930
I 2	.1992	.36350
II 2	.2000	.36534
I m	.3135	.5692
II m	.4222	.7643
I m	.5062	.9133
	n-Butanol	
III 1	0.01066	0.01985
III 1	.02002	.03771
II m[a,b]	.02021 .02021 .02021	.03745
I 1	.02028	.03786
III 2	.02397	.04453
III 2	.03405	.06273
II 1	.04933	.09106
I 2	.05069	.09325
III 2	.05814	.10712
I 1	.05820	.10712
I 2	.09549	.17501
III 3	.10095	.18475
II 2	.10196	.18678
III 2	.14306	.26137
I 3	.14696	.26753
I 3	.17459	.31781
III 1	.2015	.36539
III 3	.2017	.36621
III m	.2471	.44689
II m	.3306	.5946
III m	.4061	.7266
II m	.4812	.8572
	i-Butanol	
1	0.00984	0.01845
1	.01127	.02124
1	.02089	.03852
1	.02365	.04347
1	.02738	.05060
1	.02769	.05126
1	0.03007	0.05580
1	.03656	.06762
1	.04104	.07572
1	.05077	.09346
1	.05901	.10880
1	.06777	.12434
2	.07808	.14417
1	.10004	.18291
1	.13623	.24862
1	.17574	.31960
	s-Butanol	
3	0.01031	0.01908
3	.02098	.03900
2	.02964	.05468
2	.04085	.07532
3	.06032	.11135
1	.06842	.12577
3	.08049	.14764
2	.10130	.18653
3	.11921	.21859
4	.12609	.23062
2	.15377	.28130
2	.2084	.37997
	t-Butanol[c]	
3	0.02099	0.03902
3	.03957	.07338
3	.05919	.10992
3	.08059	.14911
3	.11037	.20437
3	.14932	.27590
	i-Pentanol[d]	
1	0.02571	0.04710
2	.05014	.09137
1	.09947	.18118
	Benzyl Alcohol[e]	
1	0.02484	0.04535
1	.02955	.05396
2	.05320	.09682
1	.07740	.13979
1	.10067	.18082

[a] In these tables samples designated *m* denote mixtures of the other samples or fractions.

[b] Over five liters of this solution were made up and three independent runs made with it. Hence the weight to be attached to these values is greater than that of the other single determinations.

[c] Only fraction 3 was used in these solutions. The other fractions all had freezing points lower than that of the third. Solutions made with fractions 2 and 4 gave values of *j* somewhat lower and higher, respectively, than those with fraction 3 at corresponding concentrations.

[d,e] These substances were used in order to find out if the cryoscopic behavior is markedly different for solutes near the limit of solubility.

Summary

A fairly rapid method is described for measuring the molal lowering of the freezing point in dilute aqueous solutions of non-electrolytes. The method is checked by obtaining values for the depression in solutions of lead nitrate, sodium chloride and mannitol, and an accuracy of about one part in a thousand is estimated for the cryoscopic results. Data are given for nine aliphatic alcohols and for benzyl alcohol over a range of concentration from 0.01 to 0.5 molal for four primary alcohols, and from 0.01 to 0.2 molal for the others.

PRINCETON, N. J. RECEIVED JANUARY 13, 1934

NOTES

Thermodynamic Dissociation Constant of a Weak Base

BY ELLIOTT J. ROBERTS

The thermodynamic dissociation constant of a weak base may be determined by any one of several galvanic cell arrangements without liquid junctions.[1] The purpose of this paper is to describe a new method which has the same advantages of simplicity of extrapolation which characterize the method used by the writer in the determination of the K_w of water.[2] The essence of the method was the measurement of two electrodes of the second kind directly against each other in a common solution containing ions requisite to the reversibility of both electrodes. In such cells, when monovalent ions alone are involved, the extrapolation to give the E° of the cell is linear with the ionic strength for a considerable range and is generally of slight slope.[2,3]

The above method does not apply to weak bases (except in the case of amphoteric electrolytes),[1c] since the electrode involving the base is of the third kind. However, by inserting an electrode of the first or third kind in place of the silver chloride electrode, the same simple extrapolation should result. Except for alkali and alkali earth metal electrodes, which require dropping electrodes and reference cells, the thallium electrode appears to be the only one of the first kind which

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[1] (a) Harned and Robinson, THIS JOURNAL, **50**, 3157 (1928); (b) Harned and Owen, *ibid.*, **52**, 5091 (1930); (c) Owen, *ibid.*, **56**, 24 (1934).

[2] Roberts, *ibid.*, **52**, 3877 (1930).

[3] Harned and Ehlers, *ibid.*, **54**, 1350 (1932); *ibid.*, **55**, 2379 (1933); Nims, *ibid.*, **55**, 1946 (1933); MacInnes and Belcher, *ibid.*, **55**, 2630 (1933).

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

$$\mathrm{Tl(Hg)} \mid \mathrm{TlClO_4}(m_1),\ \mathrm{BClO_4}(m_2),\ \mathrm{BOH}(m_3) \mid \mathrm{H_2} \quad \text{(A)}$$

where BOH is a weak base. The potential of the cell is given by the equation

$$E = E^\circ - \frac{RT}{F} \ln \frac{[\mathrm{Tl^+}][\mathrm{BOH}]}{[\mathrm{B^+}]} p_{\mathrm{H_2}}^{1/2} - \frac{RT}{F} \ln K_b - \frac{RT}{F} \ln \frac{\gamma_{\mathrm{Tl^+}}\ \gamma_{\mathrm{BOH}}}{\gamma_{\mathrm{B^+}}\ (\mathrm{H_2O})} \quad (1)$$

where

$$E^\circ = E^\circ\ \mathrm{Tl(Hg)},\ \mathrm{Tl^+} - E^\circ\ \mathrm{H_2},\ \mathrm{H_2O},\ \mathrm{OH^-} \quad (2)$$

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

$$\ln K_b + \ln \frac{\gamma_{\mathrm{Tl^+}}\ \gamma_{\mathrm{BOH}}}{\gamma_{\mathrm{B^+}}\ (\mathrm{H_2O})} = \frac{E^\circ - E}{RT/F} - \ln \frac{[\mathrm{Tl^+}][\mathrm{BOH}]}{[\mathrm{B^+}]} p_{\mathrm{H_2}}^{1/2} \quad (3)$$

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 $\mathrm{Tl^+}$ and $[\mathrm{B^+}] = [\mathrm{BOH}]$, K_b must be less than about 10^{-6}. For stronger bases, $[\mathrm{Tl^+}]$ and $[\mathrm{BOH}]$ 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.

THE DORR CO., INC.
WESTPORT, CONN.

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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.

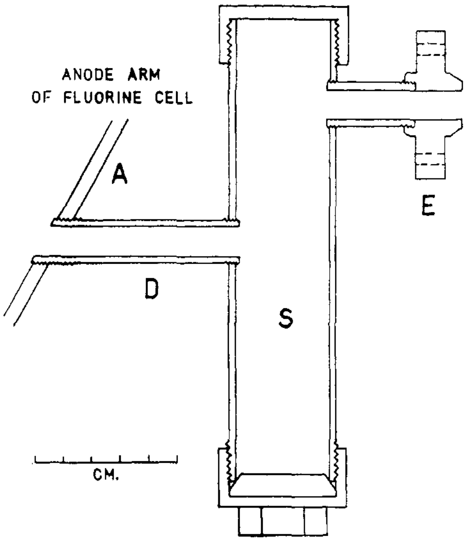

Fig. 1.

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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