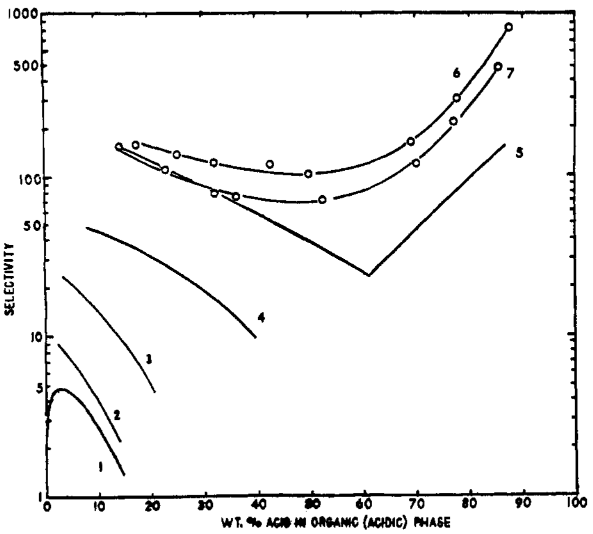

Figure 3. Selectivities in furfural–water–acid systems

1. Formic acid, 25°C (8)
2. Acetic acid, 25°C (5)
3. Propionic acid, 25°C (5)
4. Butyric acid, 25°C (3)
5. Valeric acid, 25°C (4)
6. Caproic acid, 25°C
7. Caproic acid, 35°C

A, *B*, *C* were, respectively, the wt % of furfural, water, and acid, and 1 and 2 were the organic (acidic) and aqueous phases. Both Equations 2 and 3 were nonlinear there, with the indication of possible discontinuous first derivatives in the plot. The Bachman relationship, Equation 1, was linear. The present system behaved similarly, with a slope and intercept (least-squares procedure) from the ternary tieline data of, respectively, 91.39 and 0.39 for Equation 1. The plot of Equation 1 for both the valeric and caproic acid systems is given in Figure 2, with data for both systems falling nearly on the same line.

The effectiveness of the extraction of a solute by a solvent was given by the selectivity (*12*), which in the present work may be considered as the ability of furfural to separate water and acid. Then the selectivity may be defined here as either B_2C_1/B_1C_2 or the equivalent ratio in wt % units. The selectivities in the caproic acid system at 25° and 35°C, and of the other acid systems at 25°C are given in Figure 3. The selectivity was generally greatest in the caproic acid system, but it became approximately equal for the caproic and valeric acid systems at low acid concentration. The sharply intersecting branches of the selectivity curve for the valeric acid system were replaced by a gradual shift in curvature for the caproic acid system, reflecting a like difference in the shapes of the curves for the acidic phases of the binodal curves.

For *n*-alkanoic acids in water, pK_a values varied only slightly with increasing chain length, excepting formic acid (*7*). Thus the trend is distribution behavior of the *n*-alkanoic acids between furfural and water may be ascribed essentially to variation in acid chain length rather than to variation in acid strength.

LITERATURE CITED

(1) Bachman, I., *Ind. Eng. Chem., Anal. Ed.*, **12**, 38 (1940).
(2) Hand, D. B., *J. Phys. Chem.*, **34**, 1961 (1930).
(3) Heric, E. L., Blackwell, B. H., Gaissert, L. J., III, Grant, S. R., Pierce, J. W., *J. Chem. Eng. Data*, 11, 38 (1966).
(4) Heric, E. L., Langford, R. E., *ibid.*, **17**, 209 (1972).
(5) Heric, E. L., Rutledge, R. M., *ibid.*, **5**, 272 (1960).
(6) "International Critical Tables," Vol. VII, p 40, McGraw-Hill, New York, NY, 1930.
(7) Kortüm, G., Vogel, W., Andrussow, K., "Dissociation Constants of Organic Acids in Aqueous Solution," pp 240–9, Butterworths, London, 1961.
(8) Langford, R. E., Heric, E. L., *J. Chem. Eng. Data*, **17**, 87 (1972).
(9) Othmer, D. F., Tobias, P. E., *Ind. Eng. Chem.*, **34**, 693 (1942).
(10) Quaker Oats Co., Chicago, IL, *Bull. 203-B*, p 4., (1968).
(11) Skrzec, A. E., Murphy, N. F., *Ind. Eng. Chem.*, **46**, 2245 (1954).
(12) Treybal, R. E., "Liquid Extraction," 2nd ed., p 43, McGraw-Hill, New York, NY, 1963.

RECEIVED for review March 23, 1972. Accepted April 29, 1972.

Emf Measurements on Lewis and Sargent Cells with Free Diffusion Boundaries

CHANG-HWEI CHEN
Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa. 15213

Electromotive force (emf) measurements on Lewis and Sargent cells with free diffusion type of static liquid junctions are presented. The cells studied employed Ag, AgCl electrodes and included liquid junctions between 0.100*M* KCl and 0.100*M* NaCl, 0.010*M* KCl and 0.010*M* NaCl, 0.100*M* HCl and 0.100*M* KCl, 0.010*M* HCl and 0.010*M* KCl, and 0.100*M* KCl and 0.100*M* LiCl. The measured emf's are 4.585, 4.496, 28.545, 26.408, and 7.137 mV, respectively, and are reproducible and constant to better than 0.040 mV.

It is well known that accurately reproducible results can be obtained in the measurement of a cell with liquid junction in which solutions of the same electrolyte, at different concentrations, are present on the two sides of the boundary. Measurement of concentration cells with transference is a standard method for determination of activity coefficients of electrolytes (*1*, *7*). On the other hand, the measurement of a cell potential with a heterionic junction involving different ionic species on the two sides of the boundary has generally proved to be unsatisfactory and to depend on the manner in which the junction is formed. For example, the cell potential of the junction, HCl (0.1*M*) : KCl (0.1*M*), at 25°C was reported to have values in the range of 26.78–28.27 mV (*11*), depending on the type of junction and the method of measurement.

Lamb and Larson (*9*) extensively studied the liquid junction potential and concluded that results with static liquid junction were unsatisfactory and therefore proceeded to develop the flowing junction. MacInnes and Yeh (*13*) modified their apparatus and obtained constant potentials for cells containing two solutions of the same concentration and with a common ion as in Lewis and Sargent Cells (*10*). Roberts and Fenwick (*14*) also developed a simple flowing junction and found that the result for 0.1*M* HCl : 0.1*M* KCl was "in fair accord" with the measured value of MacInnes and Yeh (28.00–26.78 mV). From the results of previous workers, it was found that for a given piece of apparatus, the flowing junction gave reproducible potentials at constant rate of flow, but the values differed for different pieces of apparatus and varied with the rate of flow. In the study of the junction between saturated KCl and different concentrations of hydrochloric acid, Ferguson and coworkers (*2*) described a method to show that reproducible and constant potential could also be obtained with a static liquid junction. The effect of the nature of the junction on the value, stability, and reproducibility of the measured emf was discussed in detail by Guggenheim (*5*). He concluded that the constrained diffusion junction was difficult to realize experimentally, and that the continuous mixture junction was theoretically unstable, though it was realized experimentally and a reproducible and constant emf was obtained. The flowing junction was assumed to be a special case of the continuous mixture junction. He also reported that the free diffusion junction was easily realized experimentally and that its measured potential was reproducible and constant to within 0.2 mV.

In connection with a computer simulation study (*4*) of the potential of a Lewis and Sargent cell—i.e., one consisting of a junction involving different electrolytes, both at same concentration and with one ion in common as expressed in cell *A*,

$$\underset{E_1}{\text{Ag–AgCl}} \,\vdots\, \text{MCl (c)}, \underset{E_J}{} \text{NCl (c)} \mid \underset{E_2}{\text{AgCl–Ag}} \qquad (A)$$

it was required to know the experimental emf's of the cells under discussion. The present work was therefore undertaken in an attempt to prepare a free diffusion type of static liquid junction in such a manner as to give measured potentials more constant and reproducible than have previously been reported. The cell potentials studied included liquid junctions between KCl and HCl, KCl and NaCl, and KCl and LiCl.

EXPERIMENTAL

Materials. Water used for recrystallization of compounds, preparation of solutions, and rinsing of cell and electrodes was obtained by passing distilled water through two Illco-Way ion exchanger columns and then through a 1-m column packed with Fisher Rexyn 300 (H–OH) resin. This water had a specific conductivity of $1-2 \times 10^{-7}$ ohm^{-1} cm^{-1}. Baker-analyzed reagents KCl and NaCl were recrystallized twice from water-ethanol mixtures, respectively, and then dried in a vacuum oven at 120°C for two days. Baker-analyzed reagent LiCl was also recrystallized from water and then stored in a dry box. Anachemia standard volumetric solution was used to prepare 0.100 and 0.010*M* HCl. The concentrations of the solutions were checked by both Volhard method and acid-base titration. City Chemical purified grade $KAg(CN)_2$ was recrystallized twice from hot water. The solution used for silver plating the electrodes was prepared by dissolving 10 grams of the dried product in a liter of water.

Electrodes. The Ag, AgCl electrodes were of the type described by Thompson (*19*), and consisted of platinum discs of approximately 1 cm in diameter on which first a layer of silver and then one of AgCl was deposited electrolytically. The electrode pairs used for cell measurement were ones which had a bias potential less than 0.030 mV in 0.10 or 0.01*M* KCl which was constant to about 0.005 mV over a 1-day period. Taking the electrode polarity into consideration, one must subtract from the measured potential the average of the bias potentials before and after cell measurement to get a correction.

Apparatus and Procedure. All solutions except HCl were prepared by weight and stored in and dispensed from 500- or 1000-ml Erlenmeyer flasks. The flask had a ground joint on the top and was covered by a proper size cap through which a delivery tube extended to the bottom of the flask. Solution was dispensed by applying nitrogen gas pressure to the solution through a side vent in the cap. The emf cell was of a type developed in this laboratory by Verrall (*20*), Rupurt (*16*), and Ku (*8*) and is shown diagrammatically in Figure 1. By turning the three-way stopcock *F* to position *IJ*, the right-hand side of the cell was filled with the less dense solution by the addition of solution directly from the flask through the electrode compartment. The stopcock was then closed when the filling was completed. An Ag, AgCl electrode was then inserted into the electrode compartment, forcing solution up the side arm.

Similarly, by turning the stopcock to position *HJ*, the left-hand side of the cell was filled with the denser solution, and an electrode was inserted. When the filling of both sides of the cell was completed and the electrodes were in position, the stopcock, *F*, was closed and both sides of its glass jacket were covered with the proper size caps. The cell was then transferred to a 25 ± 0.003°C oil thermostat for temperature equilibration, and the side tube stopcocks, *B*, were opened.

After at least 1 hr for thermal equilibration, the cell was unclamped and raised from the bath, one of the stopcocks, *B*, was closed, and the stopcock, *F*, was then very carefully turned to

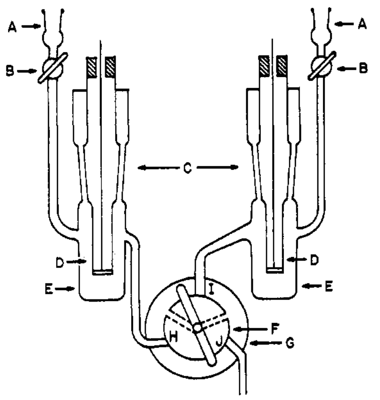

Figure 1. Cell design for concentration cell with transference

A.	10/30 Glass joint	*E.*	Electrode compartment
B.	Teflon stopcock	*F.*	Teflon stopcock
C.	19/38 Glass joint	*G.*	Glass jacket
D.	Ag, AgCl electrode	*I.*	Liquid junction

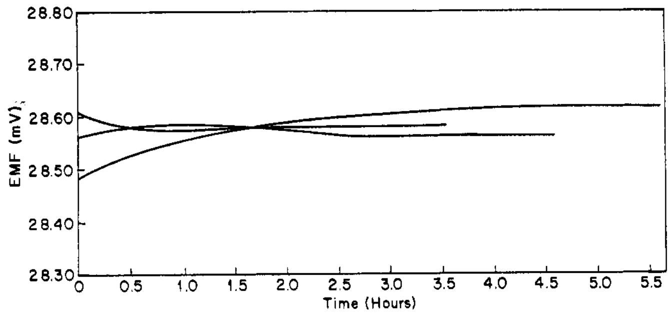

Figure 2. Change of observed emf with time in a typical measurement on the cell Ag–AgCl/HCl (*M* = 0.1), KCl (*M* = 0.1)/AgCl–Ag

Table I. Emf's of Various Lewis and Sargent Cells

Junction	E_{meas}, mV This work	Ref *13*	E_{calc}, (mV)
KCl (c):NaCl (c) (c = 0.100*M*)	4.585 ± 0.005	6.42	4.85
KCl (c):NaCl (c) (c = 0.010*M*)	4.496 ± 0.004	5.65	4.51
HCl (c):KCl (c) (c = 0.100*M*)	28.545 ± 0.039	26.78	28.51
HCl (c):KCl (c) (c = 0.010*M*)	26.408 ± 0.026	25.73	27.49
KCl (c):LiCl (c) (c = 0.100*M*)	7.137 ± 0.006	8.76	7.63

the position *HI*, thus forming the liquid junction between the two solutions at position *I*. The junction stopcock was then recapped and the cell carefully resubmerged and clamped in the oil bath. The potential measurement was then begun by means of a calibrated digital voltmeter which read to 1 μV (Hewlett-Packard model 3450A multifunction meter). The cell potential was read at 30-min intervals until it had been constant to within a few microvolts for at least 2 hr.

RESULTS AND DISCUSSION

The variation of measured emf with time for a typical case is shown in Figure 2. After an initial period of instability, the potential became constant to within 0.005 mV. These steady potentials were usually observed for more than 2 hr. If the proper precaution was not taken in turning the stopcock to form the liquid junction, there would be an initial surge of mixing of the solutions at the junction. This would produce no constant potential. The time for the potential to reach constancy after the formation of the junction depended on the salts and was less than 2.5 hr in the present experiments. Although the shape of the curves before the steady state was reached was not reproducible as observed by Finkelstein and Verdrier (*3*) and other workers, the measured emf's were reproducible to within 0.039 mV at worst and within 0.020 mV in most cases, which are much better than the value of within 0.2 mV reported by Guggenheim (*5*).

The results are presented in Table I. Each E_{meas} is the average value of at least three runs. The total potential, E, of the Lewis and Sargent cell (*A*) can be divided into three portions, E_1 and E_2 at the two electrodes and E_J at the liquid junction (*12*), that is,

$$E = E_1 + E_2 + E_J \tag{1}$$

$$E = \left[E_{\mathrm{Ag,AgCl}}^{\circ} + \frac{RT}{F}\ln a_{\mathrm{Cl(MCl)}}\right] + \left[-E_{\mathrm{Ag,AgCl}}^{\circ} - \frac{RT}{F}\ln a_{\mathrm{Cl(NCl)}}\right] + E_J = E_J + \frac{RT}{F}\ln\frac{a_{\mathrm{Cl(MCl)}}}{a_{\mathrm{Cl(NCl)}}} \tag{2}$$

Data marked E_{calc} in Table I were computed from the Lewis and Sargent equation (*10*)

$$E_{\mathrm{calc}} = \frac{2.303\ RT}{F}\log\frac{\Lambda_{\mathrm{MCl}}}{\Lambda_{\mathrm{NCl}}} \tag{3}$$

in which $2.303\ RT/F = 59.16$ for $t = 25°\mathrm{C}$, and Λ_{MCl} and Λ_{NCl} are the equivalent conductances of solutions MCl and NCl. For 0.01*M* KCl, 0.10*M* KCl, 0.01*M* HCl, 0.10*M* HCl, 0.01*M* NaCl, 0.10*M* NaCl, and 0.10*M* LiCl, Λ is 141.27, 128.96, 411.98, 391.28, 118.53, 106.74, and 95.83 conductance units, respectively (*15, 17, 18*).

When E_{meas} and E_{calc} are compared, the use of Equation 3 produces diviations reaching more than 5% in some cases. These doubtless arise from the fact that the Lewis and Sargent equation contains approximations which are no longer justified. Among these is the assumed existence of a mixture boundary in the liquid junction and the neglect of Harned's Rule changes in activity coefficients (*6*) of MCl and NCl in the boundary. [This neglect does not contain single ion activities, since the computer simulation study (*4*) has confirmed that measurement of the potential of a Lewis and Sargent cell gives no information about them.]

Data of MacInnes and Yeh (*13*) are also listed in Table I. Their emf's are higher than the present results for KCl : NaCl and KCl : LiCl junctions and lower for the HCl : KCl junction. The differences undoubtedly reflect the special conditions which exist in the flowing junctions.

ACKNOWLEDGMENT

The author is indebted to Professor Henry S. Frank for encouragement and advice.

LITERATURE CITED

(1) Brown, A. S., MacInnes, D. A., *J. Amer. Chem. Soc.*, **57**, 1356 (1935).
(2) Ferguson, A. L., Van Lente, K., Hitchens, R., *ibid.*, **54**, 1279 and 1285 (1932).
(3) Finkelstein, N. P., Verdrier, E. T., *Trans. Faraday Soc.*, **53**, 1618 (1957).
(4) Frank, H. S., Chen, C. H., to be submitted for publication.
(5) Guggenheim, E. A., *J. Amer. Chem. Soc.*, **52**, 1315 (1930).
(6) Harned, H. S., Owen, B. B., "The Physical Chemistry of Electrolyte Solution," p 603, Reinhold, New York, N.Y., 1958.
(7) Hornibrook, W. J., Janz, G. J., Gordon, A. R., *J. Amer. Chem. Soc.*, **64**, 513 (1942).
(8) Ku, J. C., PhD thesis, University of Pittsburgh, Pittsburgh, Pa., 1971.
(9) Lamb, A. B., Larson, A. T., *J. Amer. Chem. Soc.*, **42**, 229 (1920).
(10) Lewis, G. N., Sargent, L. W., *ibid.*, **31**, 363 (1909).
(11) MacInnes, D. A., "The Principles of Electrochemistry," p 230, Dover, New York, N.Y., 1961.
(12) MacInnes, D. A., *ibid.*, p 222.
(13) MacInnes, D. A., Yeh, Y. L., *J. Amer. Chem. Soc.*, **43**, 2563 (1921).
(14) Roberts, E. J., Fenwick, F., *ibid.*, **49**, 2787 (1927).
(15) Robinson, R. A., Stokes, R. H., "Electrolyte Solutions," p 466, Butterworths, London, 1959.
(16) Rupert, J. P., PhD thesis, University of Pittsburgh, Pittsburgh, Pa., 1969.
(17) Shedlovsky, T., *J. Amer. Chem. Soc.*, **54**, 1411 (1932).
(18) Stokes, R. H., *J. Phys. Chem.*, **65**, 1242 (1961).
(19) Thompson, P. T., PhD thesis, University of Pittsburgh, Pittsburgh, Pa., 1956.
(20) Verrall, R. E., unpublished results, 1971.

RECEIVED for review March 24, 1972. Accepted May 19, 1972. This work was supported by a grant from the Office of Saline Water, U.S. Department of the Interior.