

References

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STABILITY OF LIQUID JUNCTION POTENTIALS

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The widespread use of ion selective electrodes in the most varied fields - from environment to clinical chemistry, etc, as well as renewal of interest in transference data of electrolytes obtained from emf of cells with liquid-liquid junction make it crucial to have a trustworthy method of forming that junction.

The most recent transference data obtained by the determination of the electromotive force of cells with liquid-liquid junction refer to cell vessel designs which seem to be prone to instability. Several authors use the cell vessel design which is presented by F. King and M. Spiro (1) (e.g. (2), (3)), others use the one developed by Rupert (4) and adapted by Braun and Weingärtner (5) (e.g. (6), (7), cf. Fig. 1,2.

The cell vessel design used in our work, in which the junction is formed at the middle of a capillary tube of cylindrical symmetry, was developed to obtain operational pH values (8), (9) producing very steady and reproducible values, even though there was hydrogen bubbling in both compartments. However, wearing of the ground glass of the Y taps (which

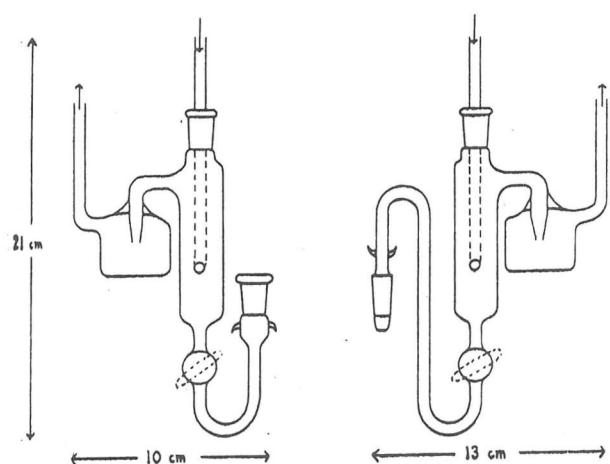


Fig. 1. Schematic diagram of the two half-cells making up the cell with transference.

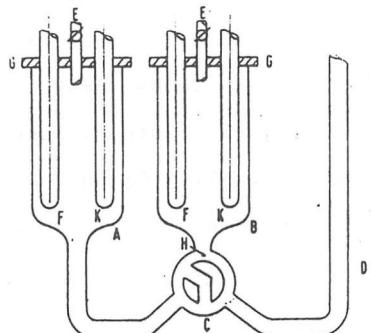


Fig. 2. Cell design for the concentration cell. A,B, electrode compartments; C, three-way stopcock; D, glass tube; E, glass tubes with stopcock; F, fluoride-selective electrodes; G, plastic caps; H, position of the liquid junction; K, potassium-selective electrodes.

interconnect the compartments) after several years of use, and the fact that some taps do not have a good quality fitness between the socket and the barrel, lead to leakage of solutions from one compartment to another. As a consequence, the slightest variation in hydrostatic head between these compartment results in values which vary from the average by 2mV or more.

Once a good quality fitness between the socket and the barrel is guaranteed, lack of stability or reproducibility of the potential of the cells can be attributed to the solutions or to malfunctioning of the electrodes. Figs. 3, 4 and 5, 6 illustrate what has been said so far.

Results

Measurements of cells

Ag AgCl	HCl	KCl	AgCl Ag	(I)
	0.09917	0.10000		
	mol kg ⁻¹	mol kg ⁻¹		

and

Ag AgCl	KCl	KCl 1.75 mol dm ⁻³	KCl	AgCl Ag	(II)
	0.09917	KNO 1.75 mol dm ⁻³	0.10000		
	mol kg ⁻¹	mol kg ⁻¹	mol kg ⁻¹		

were made at 25°C in a water thermostated bath.

The same cell vessel design was used for both cell I and II. Potassium chloride filled the middle compartment and the

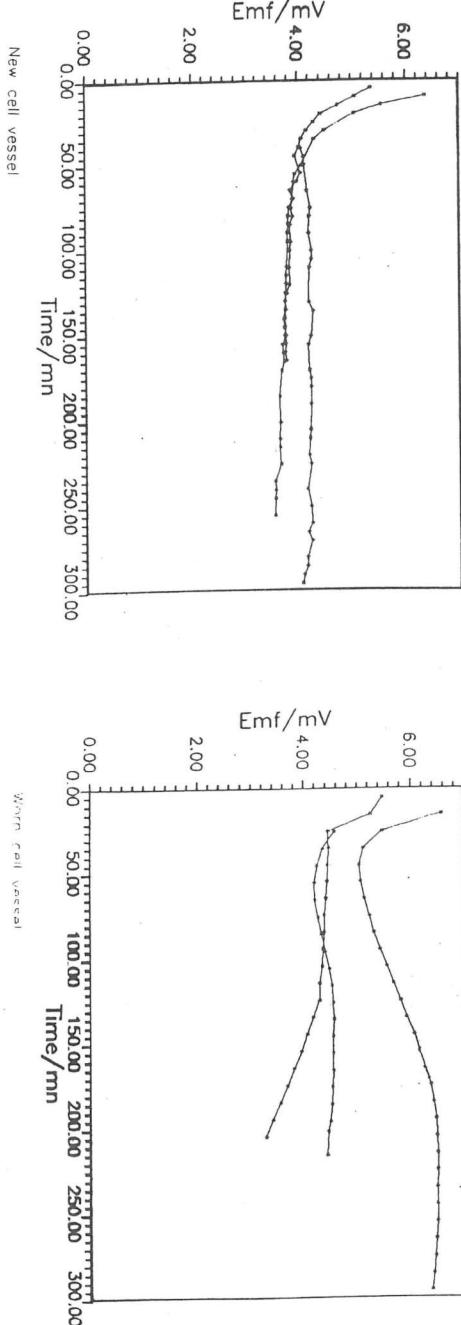


Fig. 3.

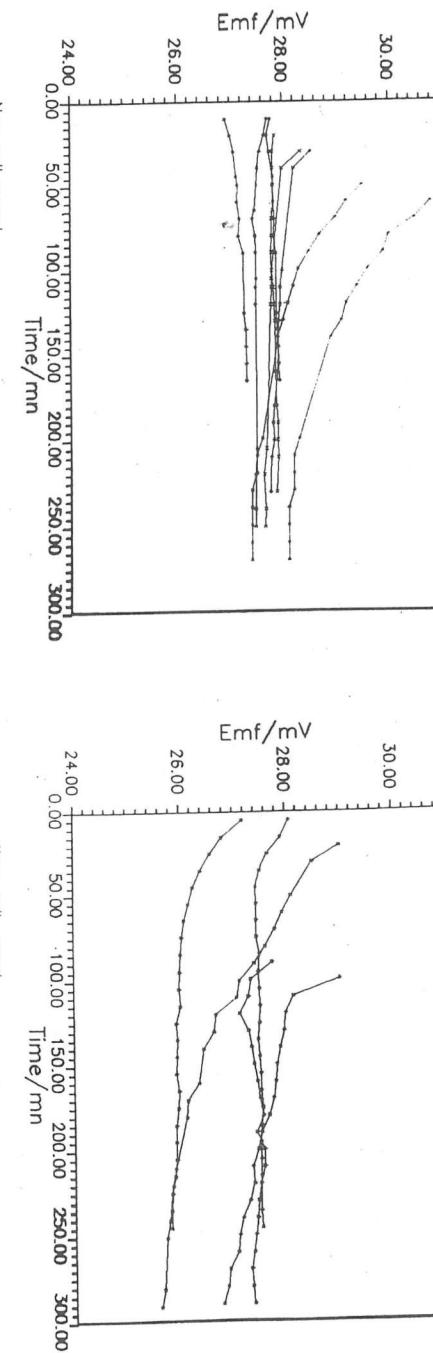


Fig. 4.

Fig. 5.

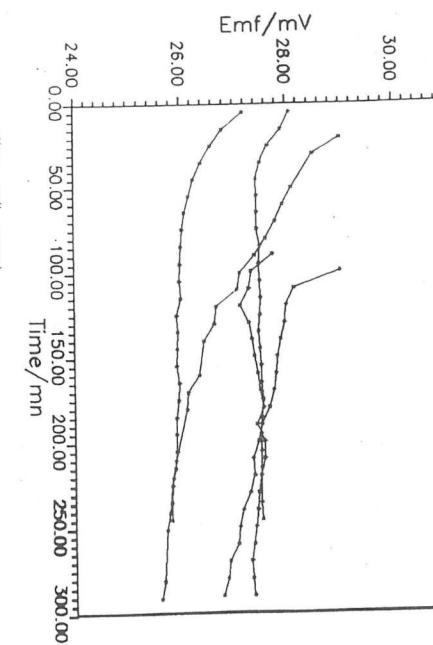


Fig. 6.

Fig. 6.

same HCl solution the other two, in cell I, thus forming two cells in one vessel.

The electrodes were prepared by the thermoelectrolytic method (10) and were conditioned in the solutions where they were to be used for ≈ 1 h before setting the cells. Transference of the electrodes straight from HCl 0.1 mole kg⁻¹ (where they are stored overnight) to the cells results in extra features in the variation of the potential of the cell with time which are due to the equilibration of the electrodes with the solution.

The observed values of the emf's of cells I and II are shown in the table.

CELL	OBSERVED		CALCULATED	
	This work	Finkelstein and Verdier	Henderson equation using activities and limiting ionic mobilities	Lewis and Sargent using molar conductivities at 0.1 mol dm ⁻³
I	27.66 ± 0.24 (average of 11 cells)	27.98	26.88	28.51
II	3.75 ± 0.44 (average of 7 cells)	4.18	3.70	-----

They compare well with Finkelstein and Verdier's (11), which were obtained with calomel electrodes and a more elaborated set up for which "the slightest mechanical disturbance was, however, enough to destroy the stability of the cell".

Conclusions

Use of the cell vessel, formerly designed to get operational pH values, with Ag/AgCl electrodes and liquid junction between HCl and KCl with and without a bridge electrolyte showed that, this is a more robust, reproducible and stable design than the previously used ones once a good quality fitness at the tap is guaranteed. This way dispersion of results can be an indication of a bias in any of the other parameters such as stability of electrodes and solutions.

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ANALISIS COMPARATIVO DE ALGUNAS ECUACIONES UTILIZADAS EN EL AJUSTE DE COEFICIENTES DE ACTIVIDAD DE MEZCLAS DE ELECTROLITOS

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Muchas han sido las ecuaciones empleadas para ajustar los datos experimentales de coeficientes de actividad obtenidos en mezclas de electrólitos [1]. Métodos teóricos sumamente complicados como los de FRIEDMAN [2-6] han dejado paso a otros semi-empíricos como los de SCATCHARD (S) [7-10], PITZER (P) [11-14] y, más recientemente, a los de LIM (L) [15-20]. Estos métodos permiten ajustar los datos experimentales a ecuaciones semi-empíricas para obtener los *coeficientes de mezcla*.

Los métodos (S) y (P) presentan problemas en cuanto al cumplimiento de la Ley Límite de Alto Orden (HOLL) [21,22]. Y así, que se cumpla o no dicha ley en el método (S) depende del procedimiento de optimización sobre el cual no tenemos control. En el método (P), al menos en su formulación inicial, (HOLL) no se cumple [22].

Para una mezcla simétrica de electrolitos 1:1, los coeficientes de actividad de cada uno de ambos electrólitos pueden ser expresados mediante las siguientes ecuaciones [17,19,21]:

$$\log(\gamma_A / \gamma_A^0) = -(y_B I/2 \ln 10) \left[g_0 + g_1(I/2 + 3YI/2) + g'_0(I/2 + YI/2) + \Phi \right] \quad (1a)$$

$$\log(\gamma_B / \gamma_B^0) = (y_A I/2 \ln 10) \left[g_0 - g_1(I/2 + 3YI/2) + g'_0(I/2 - YI/2) + \Phi \right] \quad (1b)$$

donde:

$$Y = 1 - 2y_B \quad (2a)$$

$$\Phi = (2/I) (\phi_A^0 - \phi_B^0) \quad (2b)$$

$$g'_0 = \partial g_0 / \partial I \quad (2c)$$