

This book has been prepared by the United States Department of Commerce and National Bureau of Standards in 1969 for public distribution and consumption. The purpose is to provide a basic introduction to pH and Ion Selective measurement theory and practice. As this book is now somewhat antiquated it is best suited as a historical overview for this field and a basic theoretical treatment of analytical aqueous electrochemistry.

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FORWARD

Ion Selective Electrodes represent a major advance in analytical technique. For the first time in analytical chemistry the activities of many ions can be determined quickly and conveniently in a non-destructive manner. Unfortunately, misconceptions concerning the simplicity of the method have in the past, led to some disappointments. This could have been entirely avoided if the user had been aware of what was involved in this method of analysis. This booklet has been designed to introduce the fundamental aspects of electrochemical measurement by ion-selective electrodes. Accordingly, detailed accounts of individual electrodes are not given — references to certain electrodes are only made to illustrate general principles. Further information on ion-selective electrodes can be obtained from electrode manufacturers and from publications such as "Ion-Selective Electrodes" — this book was prepared by the United States Department of Commerce, National Bureau of Standards (1969), edited by R. Durst and is recommended to anyone intending to use ion-selective electrodes.

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SOLUTION CHEMISTRY

(a) ACTIVITY VERSUS CONCENTRATION.

An ion in solution may exist as a **free ion** (i.e., not bound to other ions or molecules) or it may interact with other ions or molecules in solution. The term **ACTIVITY** of an ion "X" relates to the number of free ions of X per unit volume of solution, while the **CONCENTRATION OF X** refers to the **TOTAL** number of ions of X (i.e., free **AND** bound) per unit volume of solution. Of the two, activity is much less readily defined because in many cases we are uncertain as to the extent of interaction of X with other ions. An understanding of the relationship between activity and concentration is essential in interpreting the results of electrochemical measurements because whilst we **MEASURE** activity, we can only precisely define concentration.

(b) ACTIVITY COEFFICIENTS.

In solutions of electrolytes electrical forces acting between oppositely charged ions cause the activity of the ions to be reduced, and hence ions behave as if they were of lower concentration than that calculated from the stoichiometric concentration of the dissolved electrolyte. To obtain the activity of the ions, the concentration must be multiplied by a factor which will allow for the interionic attraction. This factor is termed the **ACTIVITY COEFFICIENT** because it gives the fraction of the total concentration which is effective in equilibrium reactions. If we represent the corrected concentration or activity by 'a'; the activity coefficient by 'f' and the concentration by 'c' then

$$a = c \times f \quad (1)$$

The value of the activity approaches that of the molar concentration or molarity as the solution is progressively diluted, since under these conditions the ions will be further apart and the interionic attraction will consequently become smaller. At infinite dilution the forces between the ions will be practically zero, $a = c$ and $f = 1$. Table (1) shows the variation of the mean activity coefficients with concentration for some electrolytes. The activity coefficient varies with valency and has the same value for all dilute solutions having the same **IONIC STRENGTH**, the latter being a measure of the electrical field existing in the solution. The ionic strength, designated by the symbol I , is defined as equal to one-half of the sums of the products of the total concentration of each ion multiplied by the square of its valency or $I = \frac{1}{2} \sum c_i z_i^2$ where c_i is the ionic concentration in gram moles/litre of solution.

Molar Concentration	0.001	0.01	0.05	0.1	0.2	0.5	1.0	2.0
HCl	0.966	0.904	0.830	0.796	0.767	0.758	0.809	1.01
HBr	0.966	0.906	0.838	0.805	0.782	0.790	0.871	1.17
HNO ₃	0.965	0.902	0.823	0.785	0.748	0.715	0.720	0.78
HIO ₃	0.96	0.86	0.69	0.58	0.46	0.29	0.19	0.10
H ₂ SO ₄	0.830	0.544	0.340	0.265	0.209	0.154	0.130	0.12
NaOH	—	—	0.82	—	0.73	0.69	0.68	0.70
KOH	—	0.90	0.82	0.80	—	0.73	0.76	0.89
Ba(OH) ₂	—	0.712	0.526	0.443	0.370	—	—	—
AgNO ₃	—	0.90	0.79	0.72	0.64	0.51	0.40	0.28
Al(NO ₃) ₃	—	—	—	0.20	0.16	0.14	0.19	0.45
BaCl ₂	0.88	0.72	0.56	0.49	0.44	0.39	0.39	0.44
Ba(NO ₃) ₂	0.88	0.71	0.52	0.43	0.34	—	—	—
CaCl ₂	0.89	0.73	0.57	0.52	0.48	0.52	0.71	—
Ca(NO ₃) ₂	0.88	0.71	0.54	0.48	0.42	0.38	0.35	0.35
CdCl ₂	0.76	0.47	0.28	0.21	0.15	0.09	0.06	—
CdSO ₄	0.73	0.40	0.21	0.17	0.11	0.07	0.05	0.04
CuCl ₂	0.89	0.72	0.58	0.52	0.47	0.42	0.43	0.51
CuSO ₄	0.74	0.41	0.21	0.16	0.11	0.07	0.05	—
FeCl ₂	0.89	0.75	0.62	0.58	0.55	0.59	0.67	—
KF	—	0.93	0.88	0.85	0.81	0.74	0.71	0.70
KCl	0.965	0.901	0.815	0.769	0.719	0.651	0.606	0.576
KBr	0.965	0.903	0.822	0.777	0.728	0.665	0.625	0.602
KI	0.965	0.905	0.84	0.80	0.76	0.71	0.68	0.69
KClO ₃	0.967	0.907	0.813	0.755	—	—	—	—
KClO ₄	0.965	0.895	0.788	—	—	—	—	—
K ₂ SO ₄	0.89	0.71	0.52	0.43	0.36	—	—	—
K ₄ Fe(CN) ₆	—	—	0.19	0.14	0.11	0.07	—	—
LiBr	0.966	0.909	0.842	0.810	0.784	0.783	0.848	1.06
Mg(NO ₃) ₂	0.88	0.71	0.55	0.51	0.46	0.44	0.50	0.69
MgSO ₄	—	0.40	0.22	0.18	0.13	0.09	0.06	0.05
NH ₄ Cl	0.96	0.88	0.79	0.74	0.69	0.62	0.57	—
NH ₄ Br	0.96	0.87	0.78	0.73	0.68	0.62	0.57	—
NH ₄ I	0.96	0.89	0.80	0.76	0.71	0.65	0.60	—
NH ₄ NO ₃	0.96	0.88	0.78	0.73	0.66	0.56	0.47	—
(NH ₄) ₂ SO ₄	0.87	0.67	0.48	0.40	0.32	0.22	0.16	—
NaF	—	0.90	0.81	0.75	0.69	0.62	—	—
NaCl	0.966	0.904	0.823	0.780	0.730	0.68	0.66	0.67
NaBr	0.966	0.914	0.844	0.800	0.740	0.695	0.688	0.734
NaI	0.97	0.91	0.86	0.83	0.81	0.78	0.80	0.95
NaNO ₃	0.966	0.90	0.82	0.77	0.70	0.62	0.55	0.48
Na ₂ SO ₄	0.89	0.71	0.53	0.45	0.36	0.27	0.20	—
NaClO ₃	0.97	0.90	0.82	0.77	0.72	0.64	0.58	—
Pb(NO ₃) ₂	0.88	0.69	0.46	0.37	0.27	0.17	0.11	—
ZnCl ₂	0.88	0.71	0.56	0.50	0.45	0.38	0.33	—
ZnSO ₄	0.70	0.39	—	0.16	0.11	0.07	0.05	0.04

TABLE (1)

Mean Activity Coefficients of Various Electrolytes

The Debye-Huckel theory of complete dissociation has provided a theoretical solution of the problem of calculating individual activities of ions in very dilute solution. The expression for the activity coefficient of an ion is:

$$\log f_i = -A z_i^2 \sqrt{I} \quad (2)$$

where z_i = valency of ion i and A depends on the temperature and the dielectric constant of the solution. The mean activity coefficient of a dilute aqueous solution of a SALT at 25° is given by:

$$\log f = -0.509 z_+ z_- \sqrt{I} \quad (3)$$

where z_+ and z_- are the valencies of the positive and negative ions respectively. The expression is a limiting one and is applicable to solutions of low ionic strength (up to about $I = 0.01$).

(c) THE pX SCALE

For many purposes, especially when dealing with small concentrations or large changes in concentration (or activities), it is cumbersome to express concentrations of ions in terms of gram equivalents per litre. A very convenient method, originally proposed for the hydrogen ion is the ion exponent (pX) defined by the relationships:

$$pX = \log_{10} [X] = \log_{10} \frac{1}{[X]} \text{ or } [X] = 10^{-pX} \quad (4)$$

The quantity pX is thus the logarithm of the reciprocal of the concentration (or activity) of X. In the case of the hydrogen ion, this method has the advantage that all states of acidity and alkalinity can be expressed by a series of positive numbers between 0 and 14.

When applied to the case (s) $X \neq H$, the p scale is less useful. The more usual measures of concentration M or ppm have been in wide use for a long time, and it is unlikely the p scale as applied to ions other than hydrogen will have much use.