CHAPTER II

THEORY

2.1 Basic Theory

2.1.1 Conductance, Transference Number and Ion-constituent

Two of the basic properties of ions in solution are conductance and transference number. Consider a solution containing ions 1, 2, ---, i. Under the influence of an applied electric field X, any ion i moves in the field direction with a constant velocity v_i such that

$$v_i \quad = \quad u_i X \qquad (2.1)$$

where u_i is the mobility of ion i which is related to the equivalent conductance of the ion λ_i by

$$\lambda_i \quad = \quad u_i F \qquad (2.2)$$

where F is the Faraday constant.

Consider an imaginary reference plane (Fig 2.1) of area a in the solution and perpendicular to the applied field X.

After time t seconds, $v_i t a\, M_i/1000$ mole of i in the volume $v_i t a$ passes across the plane, where M_i is the molar concentration of i. These ions transport an electric charge of
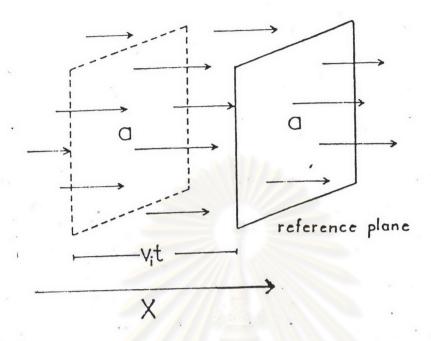
Fig. 2.1 Schematic flow diagram

$|Z_i|$ Fv_ita M_i/1000 coulomb. Total flux of charge transfered across the plane in both direction is thus,

$$\sum_i Z_i \; Fv_i \text{ta } M_i / \; 1000$$

such that the current, $I = \sum_i Z_i \; Fv_i aM_i/1000$ amperes. From Ohm's law, the conductivity K, by its definition (25) is thus,

$$K = (\sum_i Z_i \; Fv_i aM_i/1000) \; / \; aX$$

Using (2.1), $\quad K \quad = \quad \sum_i |Z_i| \; Fu_i M_i/1000$

Using (2.2), $\quad K \quad = \quad \sum_i c_i \; \lambda_i/1000$

where C_i is the equivalent concentration and

$$C_i = M_i |Z_i|$$

For a single electrolyte solution thus,

$$\Lambda C = 1000K = \overset{\Sigma}{i} C_i \lambda_i \qquad (2.3)$$

where Λ is the equivalent conductance of the solution.

Now, the number of faradays carried by ions i across the reference plane (fixed relative to the solvent) when 1 faraday of electricity, passes across that plane is the ionic or electric transport number. From above, after time t, the charge carried across the reference plane is $|Z_i| v_i taM_i/1000$ faraday. Therefore, the transference number of i is,

$$T_i = \frac{|Z_i| v_i aM_i/1000}{\sum_i Z_i v_i aM_i/1000}$$

From (2.1), (2.2) and (2.3) thus.

$$T_i = \lambda_i C_i / \Lambda C \qquad (2.4)$$

It follows that T_i is dimensionless, either positive or zero and

$$\overset{\Sigma}{i} T_i = 1$$

When an electrolyte such as KCl dissociate completely into K^+ and Cl^-, the transport properties defined above are directly obtained in practice. That is

$$\Lambda_{KCl}\, C_{KCl} = \lambda_{K^+} C_{K^+} + \lambda_{Cl^-} C_{Cl^-}$$

$$T_{K^+} = \lambda_{K^+} C_{K^+} \, / \, \Lambda_{KCl} C_{KCl}$$

$$T_{Cl^-} = \lambda_{Cl^-} C_{Cl^-} \, / \, \Lambda_{KCl} C_{KCl}$$

and

$$T_{K^+} + T_{Cl^-} = 1$$

However, a serious difficulty arises when we consider a solution in which complex ions exist ; aqueous oxalic is a typical example. This solution contains H^+, HOx^-, Ox^{2-} and H_2Ox in rapid dynamic equilibria. For this system, it is the transport properties arising from the transfer of these ions and not of those of the hydrogen and oxalate anion itself which are experimentally measurable. the above definition of the transport properties are thus insufficient to describe associated eletrolyte systems. It is essential to introduce the concept of " ion-constituent ", defined as the possible ion-forming portion of an electrolyte without reference to the extent to which it may actually exist in the dissociated state. Thus in aqueous acid the ion-constituent H^+ exists in the forms the ions H^+, the ions HOx^- and the molecules H_2Ox, while the ion-constituent Ox^{2-} exists in the form of the species Hox^-, Ox^{2-} and H_2Ox. Electrolysis of this solution results in opposing flows of positive charged ion (H^+) and negatively charged ions (HOx^-, Ox^{2-}). Consequently, only the net flows of

ion-constituents, and thus the transport properties of the ion-
constituents and not those of the individual ion can be
practically determined. This lead to the formal definition of
the transference number.

The " transference number " of a cation-or anion-
constituent is defined (6) as the net number of faradays carried
by that constituent in the direction of the cathode or anode,
respectively, across a reference plane fixed with respect to the
solvent, when one faraday of electricity passes across the plane.
Following the same situation as before, and supposing that each
mole of ion i contains $N_{R,i}$ moles of ion-constituent R, the
number of moles of ion-constituent R crossing the plane as part
of the ionic species i is therefore $N_{R,i}v_i taM_i/1000$. The
electrical charge on any ion is then the algebraic sum of the
charges of its component ion-constituents, that is,

$$\sum_R Z_R N_{R,i} = Z_i$$

Thus the net number of moles of R crossing the reference plane is

$$\sum_i \frac{Z_R}{|Z_R|} \frac{|Z_i|}{Z_i} \frac{N_{R,i}v_i taM_i}{1000} \tag{2.5}$$

The factor $|Z_i| / Z_i$ specifies the opposing directional effects
from the cations and anions carrying a given ion-constituent,
while the facter $Z_R / |Z_R|$ is required to distinguish between
cation and anion constituent. The transference number of ion-

constituent R, T_R can be obtained by multiplying (2.5) by $|Z_R|$ and dividing by the total flux of charge transferred across the plane in both directions, $\sum |Z_i| \, v_i \, taM_i / 1000$ faradays. Thus

$$T_R = \frac{\sum_i Z_R \left[\dfrac{Z_i}{Z_i}\right] N_{R,i} v_i M_i}{\sum_i |Z_i| v_i M_i}$$

Using (2.1) and (2.2) thus

$$T_R = \frac{\sum_i \left[\dfrac{Z_R}{Z_i}\right] N_{R,i} \lambda_i c_i}{\sum_i \lambda_i c_i} \qquad (2.6)$$

It can be proved that

$$\sum_R T_R = 1 = \sum_i T_i$$

2.1.2 Concentration Dependence of Transference Numbers

The equivalent conductance Λ, of completely dissociated electrolytes at low concentration is found to be a decreasing linear function of square root of concentrations. Extrapolation to zero concentration yields the limiting equivalent conductance Λ°. Thus

$$\Lambda = \Lambda^\circ - A \sqrt{M} \qquad (2.7)$$

as was first observed by Kohlrausch. The theoretical prediction of constant A was made by Onsager, from which he found that

$$\Lambda = \Lambda^{\circ} - (B_1 \Lambda^{\circ} + B_2)\sqrt{M} \quad (2.8)$$

known as the Onsager limiting law. In the equation (2.8)

$$B_1 = \frac{|Z_A Z_B| e^3}{3(Dk\,J)^{3/2}} \cdot \frac{q}{1 + \sqrt{q}} \cdot \beta$$

and

$$B_2 = \frac{|Z_A| + |Z_B|}{(Dk\,J)^{1/2}} \cdot \frac{Fe^2}{6\pi\eta} \cdot \beta$$

where $\beta = \left[\dfrac{8\pi N}{1000}\right]^{1/2} \cdot \sqrt{\dfrac{I}{M}}$ and Z_A, Z_B are valencies

of the cation and anion respectively. The Onsager limiting law equation (2.8) is still restricted to a dilute concentration range and is mostly successful for fully dissociated electrolytes.

Transference numbers are essentially ratios of conductances and so usually vary less with concentration than to conductances themselves. The concentration dependence of the transference numbers of most completely dissociated symmetrical electrolytes follows a standard pattern in dilute solutions. For these electrolytes, the transference number equation for the cation, A, becomes

$$T_A = T_A^{\circ} + \left\{ (|Z_A| + |Z_B|)\, T_A^{\circ} - |Z_A| \right\} \cdot \frac{B_2\sqrt{I}}{2\Lambda^{\circ}} \quad (2.9)$$

Equation (2.9) accurately predicts the limiting tangents for most of 1 : 1 electrolyte (11, 20) such as HCl, KCl, KI, KBr, NaCl,

NH_4Cl and CH_3COONa in aqueous solutions. It was also found that for uni-univalent electrolytes, T_A increased with concentration when it exceeds 0.5, decreased with concentration when it is less than 0.5, and changes hardly at all when it close to 0.5. In the case of higher valent-salts or unsymmetrical electrolytes for e.g Na_2SO_4 and $CaCl_2$(20), the observed T_A value do not approach the limiting slope in equation (2.9) even at extreme dilutions. For associated electrolytes, a complicated concentration dependence of the transference numbers can result. A change in the proportion of the different ionic species in solutions lead to a marked change in the transference numbers.

2.2 Theory of the moving Boundary

The moving boundary (m.b.) method is known to be the most precise technique available for determining transference numbers in solution (6). General accounts of moving boundary theory can be found elsewhere (6, 26). The theory is explained with reference to Fig 2.2, a schematic diagram of a rising boundary experiment. Suppose the boundary is first formed at position 1 between a leading solution α of an electrolyte $A_{\nu_A} Y_{\nu_Y}$

(AY in short) and a following or indicator solution β of an electrolyte $B_{\nu_B} Y_{\nu_Y}$ (BY), where M_{AY}^{α} and M_{BY}^{β} are their initial concentrations respectively.
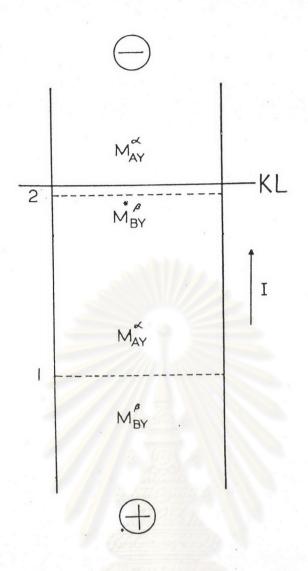
Fig. 2.2 Schematic Diagram of Rising Boundary Experiment

If a constant current I is passed through the solution in the moving boundary tube of a uniform cross-sectional area a for a time t, corresponding to f $(= It / F)$ faraday of electricity, then the boundary between the two solutions will move at a steady velocity v_b up the tube from the initial position 1 through an observed volume V_{obs} to a position 2. The effect will be to sweep out $Z_A M_A^{\alpha} V_{obs}^{\alpha \beta}$ equivalents of the ion-constituent A across the imaginary plane KL and replace the

same amount of ion-constituent B in the region between the position 1 and 2. This gives the observed transference number of the leading non-common ion-constituent A :
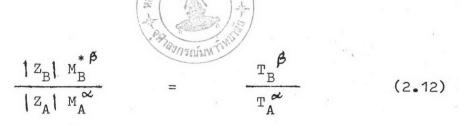
$$T_A^\alpha (obs) \quad = \quad |Z_A| M_A^\alpha v_b aF/I \quad = \quad |Z_A| M_A V_{obs} F/It \quad (2.10)$$

where Z_A is the algebraic charge number of A. This equation involves no assumptions about the degree of dissociation or the state of complexation of the electrolyte since both the transference number and concentration are properties of the ion-constituent and not of the individual ions. It is, however, a special case of a general moving boundary equation for a given ion-constituent R :

$$T_R^\alpha - T_R^\beta \quad = \quad V^{\alpha\beta} (|Z_R| M_R^\alpha - |Z_R| M_R^\beta) \frac{F}{It} \quad (2.11)$$

where R is present on both sides of a boundary (27, 28). Therefore, as $M_A^\beta \rightarrow 0$ and $M_B^\beta \rightarrow 0$, the general equation (2.11) reduces to (2.10)

In equation (2.10) the velocity of the boundary, v_b, depends upon the properties of the leading solution only and is usually independent of the type and initial concentration of the following electrolyte (or the indicator solution) within fairly wide limits if the cell is properly designed. Under a steady state condition, the concentration of the indicator solution near the boundary adjusts itself automatically to a new value such that

$$\frac{|Z_B| \, M_B^{*\beta}}{|Z_A| \, M_A^{\alpha}} = \frac{T_B^{\beta}}{T_A^{\alpha}} \qquad (2.12)$$

This is the Kohlrausch equation and $M_B^{*\beta}$ is the Kohlrausch concentration which usually differs from the initial concentration M_B^{β}. The extent of this adjustment was demonstrated with the aid of schlieren scanning camera by Longsworth (29). It was experimentally observed that under the influence of a constant current, such that the moving boundary moves with a steady velocity v_b, the concentration distribution M_R of any ion-constituent R in the neighbourhood of the boundary remained constant as a function of coordinate x (distance along the tube) and time t of electrolysis. That is

$$M_R = f_R \, (x - v_b t)$$

It follows from the equation of continuity (26, 29) and integration that

$$M_R v_b = M_R v_R + K_R$$

where v_R is the linear velocity of R relative to the cell and K_R is a corresponding integration constant.

For the system where the non-common ion-constituent disappear across the boundary i.e. $M_A^{\beta} = 0$ and $M_B^{\alpha} = 0$ in the pure β and α phase respectively, $K_A = K_B = 0$ such that

$$v_b = v_A = v_B$$

That is, the indicator ion-constituent at the boundary must move at the same rate as the leading ion-constituent. This can occur only at one concentration for a given concentration of the leading solution. Therefore, under a steady state condition, the automatic adjustment must be achieved and the Kohlrausch equation (2.12) must hold.

The moving boundary equation require volume corrections to convert the quantities derived relative to the moving boundary cell to those relative to solvent reference frame. This fundamental point was first recognized by Lewis (30). However most of the following work used the assumption about the constant partial molar volume of solvent which was experimentally unjustified. Recently, Gwyther and Spiro (12) have pointed out that this difficulty can be overcome simply by returning to the original method of Lewis and employing apparent molar volumes instead of partial molar volumes. A detailed account of the volume correction employing apparent molar volumes for the equation (2.10) and (2.12) was then given. Any changes in the partial molar volume of the solvent ($\bar{\Phi}_0$) are automatically taken care of within the apparent molar volumes of the solute (Φ). This follows from the basic equation for the volume V of a binary solution containing n_0 mole solvent and n_{AY} mole solute :

$$V = n_o \bar{\phi}_o + n_{AY} \bar{\phi}_{AY} = n_o \bar{\phi}_o^o + n_{AY} \bar{\phi}_{AY}$$

$$1 = M_o \bar{\phi}_o + M_{AY} \bar{\phi}_{AY} = M_o \bar{\phi}_o^o + M_{AY} \bar{\phi}_{AY}$$

where $\bar{\phi}$ denotes partial molar volume

and $\bar{\phi}_o^o$ is the molar volume of pure solvent

The Kohlrausch equation (2.16) was therefore corrected to

$$\frac{T_B^\beta}{T_A^\alpha} = \frac{|Z_B| M_B^{*\beta} (1-M_{AY}^\alpha \bar{\phi}_{AY}^\alpha)}{|Z_A| M_A^\alpha (1-M_{BY}^\beta \bar{\phi}_{BY}^\beta)} = \frac{|Z_B| M_B^{*\beta}/M_o^\beta}{|Z_A| M_A^\alpha /M_o^\alpha} = \frac{|Z_B| m_B^{*\beta}}{|Z_A| m_A^\alpha} \qquad (2.13)$$

where m denotes the molal concentration. Equation (2.13) reconciles those derived by Bearman (31), Milios and Newman (32), Smits and Duyvis (33) and Hartley (8).

The volume corrected Kohlrausch equation (2.13) is also subject to a solvent correction. This correction will be discussed in the method of analysis.

2.3 Determination of the Transference Numbers by the Indirect Moving Boundary Method.

There are two main applications of moving boundary theory to transference number measurements. One is refered to as the direct moving boundary method. In this method, an electric current maintains and moves a fairly sharp boundary between the solution under investigation (the leading solution) and a solution of a suitable following solution. The volume traversed by the boundary is measured when a known quantity of electricity has passed

through both solutions. The observed transference number of the leading ion-constituent can be calculated from equation (2.10). The indirect moving boundary method is complementary to the former method in that the solution following the boundary is the solution under investigation. The transference number in this solution is determined by measuring the adjusted or Kohlrausch concentration behind the boundary and making use of equation (2.12) or (2.13). Indeed, the method has sometimes been called the adjusted indicator technique (9).

General experimental precautions for the moving boundary technique have been discussed by various authors (6, 26). The conditions for the boundary stability and other experimental requirements are summarised as follow.

2.3.1 Condition for Boundary Stability

Stable boundaries are required for moving boundary experiments. Their existence may be understood by considering the so-called electrical restoring effect (6, 26, 34). With reference to Fig 2.2, this effect operates automatically whenever the mobility of the leading non-common ion-instituent A is greater than that of the following constituent B in both solutions and in any possible mixture of them (6, 34). That is

$$u_A^\alpha > u_B^\alpha$$

$$u_A^\beta > u_B^\beta$$

$$\text{and} \quad u_A^{\alpha\beta} > u_B^{\alpha\beta}$$

where $\alpha\beta$ refers to a mixed phase. In most cases, the passage
of current will cause a greater potential drop in the following
solution than in the leading solution. This is also shown
diagrammatically in the Fig. 2.3, where values of the electromotive
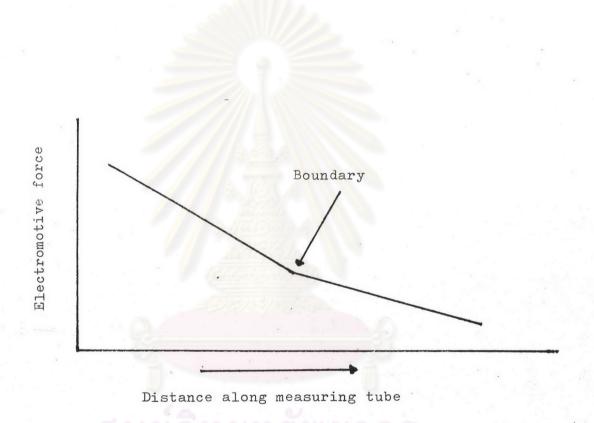force are plotted as ordinates and distance along the measuring
tube as abscisae.

Fig. 2.3 Distribution of e.m.f in the region of a moving boundary

Now if diffusion or convection occurs, any ion-constiuent
A may drift into the BY solution, they will encounter a high
potential gradient and will be sent forward to the boundary.
On the other hand, if any trace of ion-constituent B diffuses
or is carried by convection into the AY solution, it will

experience a lower potential gradient and move slower than ion-constituent A nearby, and will finally be overtaken by the boundary. This requires that

$$u_A E^\beta \; > \; v_b \; > \; u_B^\alpha E^\alpha$$

when E^α and E^β are potential drops in solution α and β respectively. Under suitable experimental conditions, a steady state can be achieved by this rectifying action counteracting the convective and diffusive mixing.

Boundaries possess a small but finite thickness, of the order of 0.01 cm. McInnes and Longsworth (26) have derived an equation for this thickness :

$$\delta \;\; = \;\; \frac{4\,R\,\mathcal{J}}{F v_b} \cdot \frac{u_A u_B}{(u_A - u_B)}$$

It is obvious that the greater the difference between the mobilities of the leading and following ion-constituents, the sharper and faster the boundary. High current therefore sharpens the boundary. In weak electrolytes however, other factors may come into play, the pH or association effect which causes the mobility of an ion-constituent to change across the boundary.

It is therefore essential to recognise the possible disturbing effects which may destroy the boundary stability. Many experimental investigations have been carried out to develop suitable experimental conditions. Certain disturbing

factors can be largely eliminated by proper design of apparatus and suitable technique.

2.3.2 Experimental Conditions

The indirect moving boundary method requires the usual moving boundary conditions as well as precise analysis of the indicator solution.

Disturbances

1. Gravitational or density gradient. For rising boundaries, the following solution must have higher density than the leading solution and for the falling boundaries the reverse must hold. It has been suggested that, for rising boundaries, initial indicator concentrations should be equal to or greater than the Kohlrausch concentration so that the system is gravitationally stable. For falling boundaries it is safer to use initial concentration equal to or less than the Kohlrausch concentration.

2. Diffusion. This arises from the concentration gradient around an electrode or in the vicinity of the concentration boundary. Diffusion influence the thickness of the boundary but not its rate of motion. Any interference can be reduced by increasing the length of the cell and decreasing the time of electrolysis. This point is very important for the analysis of the indicator solution in the indirect method.

3. Joule heating sets up a radial temperature distribution with maximum temperature at the axis of the moving

boundary tube and the resulting density differences cause convective mixing. This disturbing effect can be decreased by using tubes of small bore (i.d. between 5-2 mm) and the current is kept small ($<$5 mA). In solutions of low conductivity (low concentration, ion association) temperatures may rise by several degree so the transference numbers must be measured at several values of current and extrapolated of zero current. A twofold current variation should be investigated for every system and the results of the transference numbers remain constant.

4. Temperature gradient across the boundary. During a determination heat is developed in the measuring tube and the following solution is normally hotter than the leading solution. Thus the two solutions meeting at the boundary are at slightly different temperature. The temperature gradient between them sets up thermal convection of the solutions in the vicinity of the boundary. This effect may be offset by the restoring action depending on the properties of the solution and the current.

5. Mechanical vibration of the apparatus may be avoided by mounting the cell separately from other mechanical devices. It has been shown that the boundary stability towards mechanical influences is greater in a tube with small bore than in a wider tube (35).

6. Electrical migration of ions introduced by the electrode reactions to the middle compartment can be reduced by increasing the volume of electrode vessels, which a certain distance away from the middle section. A minimal interference

from hydrolysis in either solution is required to allow precise
analysis of solution.

2.3.3 Analytical Method

One of the most important basic requirements of the
indirect moving boundary technique is the analytical method of
determining the indicator concentration behind the boundary (6).
External or internal analysis has been used with suitable
techniques for the determination of the Kohlrausch concentration.
Among them, conductometric (8, 9, 10), interferometric (36) and
the potentiometric (13) analysis have been prominent.   The
refractometric method (29) have been mostly limited to the use
of Tiselius cell for the study of multicomponent systems.
Details of these methods can be read eleswheres (6, 8, 9, 10, 29)

Muir, Graham and Gordon (10) pointed out that the
Kohlrausch relation required a solvent correction. They consider
a KCl/NaCl system which gave results agreeing with those
obtained by the direct moving boundary method within 0.03% .
Their results were corrected for solvent impurity by carrying
out blank experiments from which they reported of amounting to
$1.10 \times 10^{-6} \ \Omega^{-1}. \ cm^{-1}$, independent of solute (NaCl)
concentration.

Recently, Gwyther and colleagues (37) have discussed
the solvent correction for the indirect moving boundary method.
The equation used by Muir, Graham and Gordon was disproved and
a new equation derived, such that

$$\frac{T_B^{\beta}}{T_A^{\alpha}} \text{(corrected)} = \frac{T_B^{\beta}}{T_A^{\alpha}} \text{(observed)} \cdot \frac{P^{\alpha}}{P^{\beta}}$$

where

$$P^{\alpha} = \frac{K_{AY}}{K_{AY} + K_{solvent}^{\alpha}}$$

similarly

$$P^{\beta} = \frac{K_{BY}}{K_{BY} + K_{solvent}^{\beta}}$$

where K refers to conductivity.

The solvent correction factor is accordingly

$$\frac{P^{\alpha}}{P^{\beta}} = \left[1 + \frac{K_{solvent}}{K_{BY}}\right]\left[1 + \frac{K_{solvent}^{\alpha}}{K_{AY}}\right]^{-1}$$

$$= 1 + \frac{K_{solvent}^{\beta}}{K_{BY}} - \frac{K_{solvent}^{\alpha}}{K_{AY}}$$

The value of $K_{solvent}$ to be used in the solvent correction is not necessarily the same as that measured on a sample of the bulk solvent. Contamination can be introduced either in the moving boundary cell or during sample analysis. For aqueous solutions the effective solvent conductivity cannot be reduced much below $1 \times 10^{-6} \ \Omega^{-1} \cdot cm^{-1}$ (37).

For the analysis of the indicator solution, it is necessary that the Kohlrausch concentration should prevail

over a fairly long section of the tube. These point have been investigated by same workers (29, 36, 37). Quantitative checks on the extent of Kohlrausch adjustment have been carried out in this work and will be discussed in detail later.

In short, the accuracy of the indirect moving boundary measurements rely on the experimental conditions and the cell design as well as the analysis. With the above precautions and several others in mind it has been suggested that (6) each system should be tested on its own merits, with respect to the determining factors.