Ion Exchange Equilibria in a Ternary System

LEONARD J. PIERONI and JOSHUA S. DRANOFF

Northwestern University, Evanston, Illinois

A study has been made of the cation exchange equilibria between Dowex 50W-X8 resin and aqueous solutions of copper nitrate, nitric acid, and sodium nitrate in binary and ternary mixtures. Experiments were carried out at room temperature with solutions having total cation concentrations of approximately 0.1N, 0.05N, and 0.01N. It was found that the equilibria for any two ions were essentially the same in binary and ternary mixtures. Moreover single valued selectivity coefficients were determined which characterize these data quite well for all three concentration levels. This makes possible the complete description, for engineering purposes, of ternary equilibria in terms of the simpler and more accessible binary exchange reactions, as previously suggested (1).

One of the controlling factors governing the use of ion exchange separations is the equilibrium distribution of ions, between resin and solution phases, which can be achieved in any given system. For this reason ion exchange equilibria have been widely studied in recent years. [See for example Kitchener (2), Kunin (3), or Nachod and Schubert (4).] With but a few exceptions however all of the previous work has dealt with exchanges in binary systems, that is those which contain only two exchanging species, or with multicomponent systems containing ions in only trace amounts.

In view of the frequent occurrence of multicomponent ionic systems in practical situations it seems desirable to extend basic equilibrium studies to systems containing more than two ions. The recent work of Dranoff and Lapidus (1) and of Smith (5) with ternary cation systems represents a start in this direction. Both of these studies demonstrated the feasibility of representing ternary equilibrium data in terms of binary systems, but only with rather limited data. The present investigation was initiated in order to test this approach more thoroughly over a reasonable concentration range. It is hoped that this will serve as a reliable guide to the eventual treatment of more complex multicomponent exchange systems.

THEORY

The theory of equilibrium in ion exchange reactions has been widely studied. It has been shown (2, 3) that in most cases the equilibria may be described in terms of either Donnan membrane equilibrium theory or standard mass action chemical equilibrium. When rigorously applied to include resin swelling and solution nonideality these two approaches lead to different equilibrium expressions (2). However if ideal solutions are assumed, as well as negligible effect due to resin swelling and hydration, they yield the same relationships.

In particular for a binary reaction of the form

$$bA_R^{a+} + aB_S^{b+} \rightleftharpoons bA_S^{a+} + aB_S^{b+} \quad (1)$$

the equilibrium distribution of ions in the resin and solution phases is described by a selectivity coefficient (concentration equilibrium constant) given by

$$K_{AB} = \frac{(c_A)^b (q_B)^a}{(q_A)^b (c_B)^a} \quad (2)$$

The solution and resin phase ion concentrations may be replaced by the more convenient equivalent fractions, x and y respectively, to yield

$$K_{A-B} = \frac{(x_A)^b (y_B)^a}{(y_A)^b (x_B)^a} \left(\frac{C_o}{Q_o} \right)^{b-a} \quad (3)$$

It should be noted that the equilibrium distribution for a uni-univalent exchange will not be affected by changes in solution concentration or resin capacity, although such changes can profoundly affect exchanges of ions with different valences.

Selectivity coefficients such as K_{AB} have been found to vary more or less, depending upon the ions in question, with resin loading and solution concentration. Although this restricts somewhat their utility for very accurate calculations, it has been possible to assign single average values to these constants which represent experimental data adequately for engineering purposes. For this reason this type of approach was used for analysis of the present data.

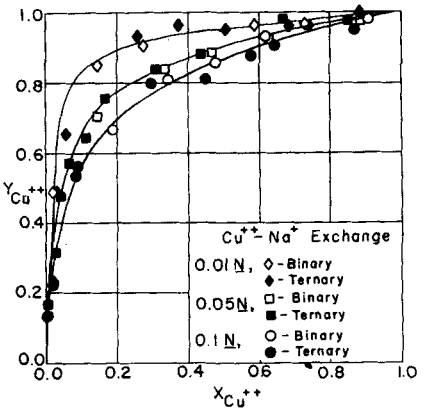

Fig. 1. Equilibria for the Cu^{++} —Na^+ exchange.

When a ternary system is considered, it is convenient to describe the exchange reactions and equilibria in terms of the various pairs of ions in the system (1). Thus for the case of the $H^+ - Na^+ - Cu^{++}$ system, one may write the following reactions:

$$H_R^+ + Na_S^+ \rightleftharpoons H_S^+ + Na_R^+ \quad (4a)$$

$$2H_R^+ + Cu_S^{++} \rightleftharpoons 2H_S^+ + Cu_R^{++} \quad (4b)$$

$$2Na_R^+ + Cu_S^{++} \rightleftharpoons 2Na_S^+ + Cu_R^{++} \quad (4c)$$

On the assumption that there will be no interactions of third ions on the various binary equilibria the equilibrium distributions will be given in terms of the binary selectivity coefficients for these exchanges. Thus

$$K_{H-Na} = \frac{(x_H)(y_{Na})}{(y_H)(x_{Na})} \quad (5a)$$

$$K_{H-Cu} = \frac{(x_H)^2 (y_{Cu})}{(y_H)^2 (x_{Cu})} \left(\frac{C_o}{Q_o} \right) \quad (5b)$$

$$K_{Na-Cu} = \frac{(x_{Na})^2 (y_{Cu})}{(y_{Na})^2 (x_{Cu})} \left(\frac{C_o}{Q_o} \right) \quad (5c)$$

It should be noted that Equations (4c) and (5c) are derivable from (4a), (4b) and (5a), (5b), respectively, and that therefore one finds

$$K_{Na-Cu} = \frac{K_{H-Cu}}{(K_{H-Na})^2} \quad (6)$$

It is clear from Equations (5) that the $H^+ - Na^+$ equilibrium should not be affected by change in solution concentration, while that for $H^+ - Cu^{++}$ or $Na^+ - Cu^{++}$ exchanges would be expected to change. These conclusions and the use of the selectivity coefficients however depend strongly on the absence of serious nonidealities in the systems at hand. Implicit in the relationships is the aforementioned neglect of resin swelling and the assumption that either activity coefficients are unity or do not change over the range of interest.

EXPERIMENTAL STUDIES

The ionic system chosen for this work was the H^+-Na^+-Cu^{++} system. These ions were selected in order to study the effect of divalent-monovalent exchange and to take advantage of relatively simple analytical methods available for two of the three ions. Aqueous solutions of the nitrates of these ions were used at three different

L. J. Pieroni is with the M. W. Kellogg Company, New York, New York. J. S. Dranoff is with Columbia University, New York, New York.

concentration levels, which were approximately 0.1, 0.05, and 0.01 normal.

The resin used was Dowex 50W-X8 in the 20 to 50 mesh size range. It had a measured capacity of 4.74 meq./g. in the dry hydrogen form (*6*).

Studies were made in the ternary system and in the three binary systems into which it may be decomposed. The equilibrium distributions of ions in the solution and resin phases were determined by simple batch contact and subsequent analysis of the final solutions. Weighed samples of resin (from 0.1 to 3.0 g.) in either the H^+ or Na^+ form were added to 100 ml. of solution of known concentration. The initial solution contained either one or both of the other two ions in the system. The samples were shaken for several hours at room temperature, and the two phases were then mechanically separated. The resultant solutions were analyzed for H^+ and/or Cu^{++} ions by physical means. H^+ ion concentrations were measured with a pH meter and Cu^{++} concentrations with a spectrophotometer with tetraethylene pentamine as the color developing agent (*7*).

The complete equilibrium compositions of both phases were calculated from the final solution analysis and the initial compositions of both phases. In these calculations the assumption of an overall material balance and the fact that the total number of equivalents in each phase remains constant during exchange was made.

RESULTS

Eighty samples were equilibrated and analyzed as described above. The number of equivalents of each ionic species present in the equilibrium mixture was calculated from the analyses by means of the material balance assumptions. A check on the validity of these assumptions was made in several binary samples containing Cu^{++} and H^+ ions. Such solutions were analyzed for both ions and the calculated total ionic concentration of the solution compared with the concentration of the starting solution used in the experiments. The results of several selected comparisons are shown in Table 1. It can be seen from these data that the assumption of the material balance is reasonable and should not lead to significant errors.

The equilibrium data obtained were considered in terms of the various pairs of ions involved in the present systems. For this purpose the data were converted into equivalent fractions of each ion in any pair present at equilibrium in the solution and resin phases. These fractions, designated X and Y respectively, are defined for the A-B exchange of Equation (1) by Equations (*7a*) and (*7b*):

Binary system	Ternary system	
$X_A = x_A$	$X_A = \dfrac{c_A}{c_A + c_B}$	(*7a*)
$Y_A = y_A$	$Y_A = \dfrac{q_A}{q_X + q_B}$	(*7b*)

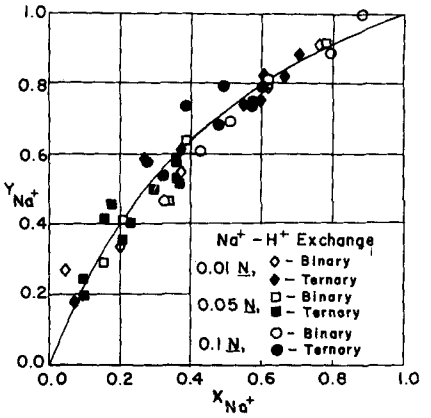

Fig. 2. Equilibria for the Na^+ —H^+ exchange.

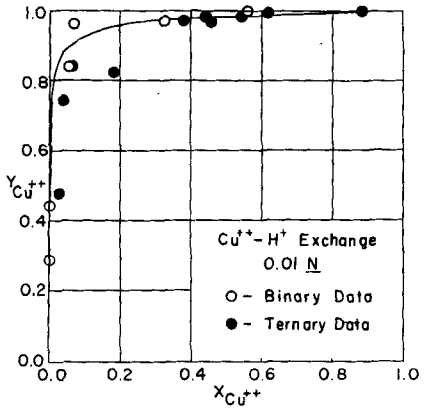

Fig. 3. Equilibrium for the Cu^{++} —H^+ exchange 0.01N.

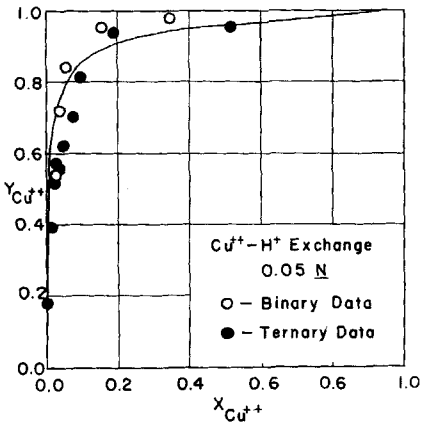

Fig. 4. Equilibrium for the Cu^{++} —H^+ exchange 0.05N.

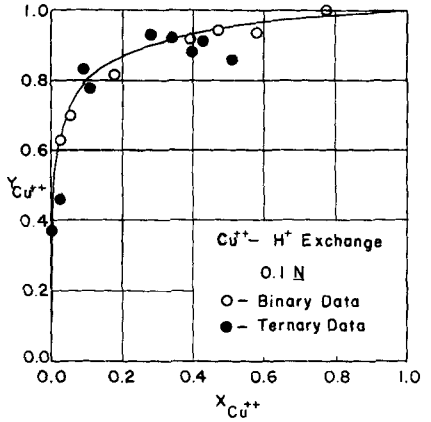

Fig. 5. Equilibrium for the Cu^{++} —H^+ exchange 0.10N.

Similar definitions would hold for the second ion in each pair.

The resultant X-Y distribution data for one of the two ions in each pair were then plotted. Both binary and ternary values were included on the same charts. The results are shown on Figures 1 to 5 for each of the three ion pairs at three different overall concentration levels. In each of these figures it is clear that binary and ternary data are essentially indistinguishable when treated in this fashion.

Selectivity coefficients were then determined from the binary data only on each chart. Data for all three concentration levels were averaged to produce the values listed in Table 2. The corresponding equilibrium curves are shown in Figures 1 to 5. Note that only one curve is necessary to describe the H^+ — Na^+ data, as shown in Equation (*5a*).

DISCUSSION OF RESULTS

The most significant result of this work is the experimental demonstration that the equilibrium distributions for several pairs of ions are the same in dilute binary and ternary systems. This confirms the previous work of Dranoff and Lapidus (*1*) which suggested that it would be possible to predict ternary equilibria from binary data alone. The study of multicomponent systems is thus significantly simplified because only binary experimental data are needed for the estimation of equilibria in more complex systems.

A second important result is the fact that a single valued selectivity coefficient can be chosen for each binary exchange which will permit a close prediction of the equilibrium distributions as shown on Figures 1 to 5. In general the data do not scatter very much from the predicted curves except perhaps for the H^+ — Cu^{++} exchange in the region of small $X_{Cu^{++}}$. Data in this region tend to be somewhat in error due to difficulties in determining very small amounts of Cu^{++} in solution.

The data behave essentially as expected with respect to changes in solution concentration level. That is the H^+ — Na^+ data show no effect of C_o, while the H^+ — Cu^{++} and Na^+ — Cu^{++} data do change with C_o exactly as predicted by Equations (5). In this connection it should be realized that in exchanges between ions of different valence the selectivity coefficient may assume values less than 1.0, even though the equilibrium may be favorable. On the other hand for ions of the same valence this is not the case. Thus for example a value of $K_{H\text{-}Na}$ equal to 2.67 indicates stronger adsorption by the resin of Na^+ than of

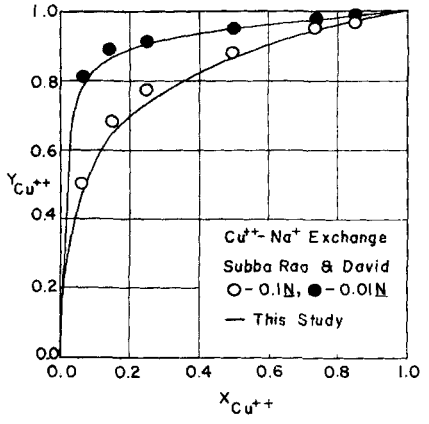

Fig. 6. Comparison of experimental and literature data for the Cu^{++} —Na^+ exchange.

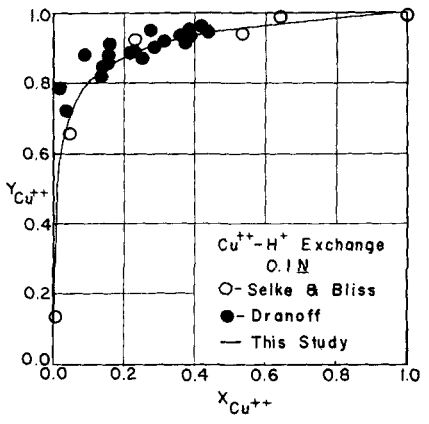

Fig. 7. Comparison of experimental and literature data for the Cu^{++} —H^+ exchange.

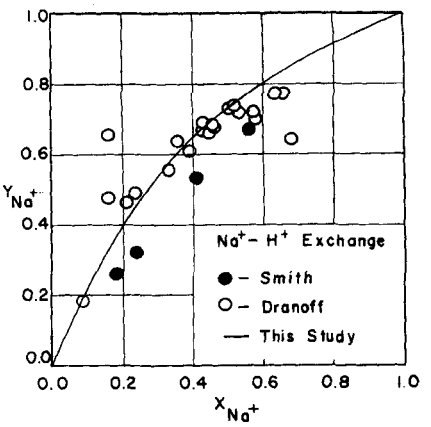

Fig. 8. Comparison of experimental and literature data for the Na^+ —N^+ exchange.

H^+, while a K_{Na-Cu} value of 0.538 indicates higher adsorption of Cu^{++} than of Na^+ for the conditions studied here.

Examination of Equations (5*a*, *b*, *c*) shows that these relations do not in general predict the superposition of binary and ternary $X - Y$ data for ions with different valences which was found. In particular when Equations (5) are transformed into these terms they become

$$K_{H-Na} = \frac{X_H Y_{Na}}{Y_H X_{Na}} \qquad (8a)$$

$$K_{H-Cu} = \frac{(X_H)^2 Y_{Cu}}{(Y_H)^2 X_{Cu}} \left[\frac{c_H + c_{Cu}}{q_H + q_{Cu}} \right] \qquad (8b)$$

$$K_{Na-Cu} = \frac{(X_{Na})^2 Y_{Cu}}{(Y_{Na})^2 X_{Cu}} \left[\frac{c_{Na} + c_{Cu}}{q_{Na} + q_{Cu}} \right] \qquad (8c)$$

Because of the actual magnitude of the selectivity coefficients and the concentration ratios in brackets in Equations (8*b*) and (8*c*), small variations in the latter do not produce significant change in the *X-Y* curves predicted by these equations. Therefore it is not possible to distinguish between the predictions of Equations (5*b*) and (5*c*) and Equations (8*b*) and (8*c*). Previously Subba Rao and David (*8*) also reported such insensitivity in studies of the Cu^{++} — Na^+ system. Note that this situation will not hold if the aforementioned ratio is increased by use of more concentrated solutions. However it is doubtful that the assumption of independent reactions would still hold under concentrated conditions in any event. As solution concentration is increased, nonidealities would become more significant, and it would no doubt be necessary to define equilibrium constants with activities or activity coefficients in order to describe the data. It is difficult to predict the limits of validity of the present approach, but it is clear that it should be used with caution in concentrated solutions. Extension to more dilute solutions should however be somewhat safer.

Table 1. Material Balance Test

Results of analysis			Starting value	
$C_{Cu^{++}}$	C_{H^+}	$C_{Cu^{++}} + C_{H^+}$	C_o	% deviation*
0.082	0.0242	0.1062	0.1060	+0.18
0.041	0.0637	0.1047	0.1060	—1.22
0.050	0.0600	0.1100	0.1060	+3.77
0.019	0.0888	0.1078	0.1060	+1.69
0.0025	0.0521	0.0546	0.0530	+3.02
0.019	0.0351	0.0541	0.0530	+2.07

*Percent deviation $= \frac{(C_{Cu^{++}} + C_{H^+}) - C_o}{C_o} \times 100.$

A comparison of the present experimental results with those of previous workers for confirmation was desired. Since no other ternary data are available for this particular system, comparisons were sought for the binary systems involved.

The Cu^{++} — Na^+ data were first compared with the results of Subba Rao and David (*8*). They studied this exchange on resin at concentrations ranging from 0.01N to 4.0N. The data for 0.10 and 0.01N concentrations are shown on Figure 6 along with the curves which correspond to the *K* value from this investigation, as reported in Table 2. The agreement is satisfactory for both curves.

The Cu^{++} — H^+ data at the 0.1N level were compared with the binary data of Selke and Bliss (*9*) and those of Dranoff and Lapidus (*1*) as measured in a ternary system. Figure 7 shows the agreement of these data with the curve from the present study. Again the agreement is good, except for low values of X_{Cu}. Note that it is difficult to get accurate data in this region, and small errors in measurements may be easily magnified in the material balance calculations.

Finally the Na^+ — H^+ equilibrium curve was compared with the ternary data of Smith (*5*) and Dranoff and Lapidus (*1*) on Figure 8. There is good agreement with the results of the latter, although the remaining data appear to differ somewhat from the present work. Previous studies of this exchange have reported lower *K* values than found here (*10*). The reasons for this are not clear, but the present data seem to be quite self-consistent and therefore acceptable.

In view of the generally close agreement found between present and previous results it seems clear that the present data are consistent with data already in the literature. Hence the experimental techniques used here are further confirmed.

CONCLUSIONS

It has been shown experimentally that equilibria in the system Cu^{++} — Na^+ — H^+ — Dowex 50 can be successfully treated in terms of the binary equilibria in the simpler Cu^{++} — Na^+, Cu^{++} — H^+, and H^+ — Na^+ systems. Close agreement between binary and ternary equilibria were found.

Furthermore it has been demonstrated that simplified binary selectivity coefficients may be used to describe these data, and that such coefficients may therefore be used in the estimation of ternary equilibria in the 0.01 to 0.1N concentration range.

ACKNOWLEDGMENT

The financial support of the Research Corporation made possible this investigation and is hereby acknowledged with thanks.

NOTATION

a, b = ionic valences
c = ionic concentration in the solution phase, meq./ml.

Table 2. Equilibrium Selectivity Coefficients

Ion pair 1	Ion pair 2	K_{1-2}
H^+	Cu^{++}	3.84
Na^+	Cu^{++}	0.538
H^+	Na^+	2.67

C_o = total ionic concentration in the solution phase, meq./ml.
K_{AB} = selectivity coefficient for exchange of ions A and B
q = ionic concentration in the resin phase, meq./g. (dry)
Q_o = total ionic capacity of the resin phase, meq./g.
x = equivalent fraction of an ion in solution phase
X = equivalent fraction of an ion in solution phase based on only two ions
y = equivalent fraction of an ion in resin phase
Y = equivalent fraction of an ion in resin phase based on only two ions

Subscripts

R = resin phase
S = solution phase

LITERATURE CITED

1. Dranoff, J. S., and Leon Lapidus, *Ind. Eng. Chem.*, **49**, 1297 (1957).
2. Kitchener, J. A., "Modern Aspects of Electrochemistry," J. O'M. Bockris, ed., No. 2, Chap. 2, Academic Press, New York (1959).
3. Kunin, Robert, "Ion Exchange Resins," 2 ed., Chaps. 2 and 3, Wiley, New York (1958).
4. Nachod, F. C., and Jack Schubert, "Ion Exchange Technology," 55, Academic Press, New York (1956).
5. Smith, N. D., Ph.D. dissertation, Ill. Inst. Technol., Chicago, Illinois (1960).
6. Pieroni, L. J., M.S. thesis, Northwestern Univ., Evanston, Illinois (1961).
7. Snell, F. D., and C. T. Snell, "Colorimetric Methods of Analysis," 3 ed., p. 120, Van Nostrand, New York (1959).
8. Subba Rao, H. C., and M. M. David, *A.I.Ch.E. Journal*, 3, 187 (1957).
9. Selke, W. A., and Harding Bliss, *Chem. Eng. Progr.*, **46**, 509 (1950).
10. Bonner, O. D., and Vickers Rhett, *J. Phys. Chem.*, **57**, 254 (1953).

Manuscript received February 7, 1962; revision received June 19, 1962; paper accepted June 26, 1962.

The Laminar-Turbulent Transition for Flow in Pipes, Concentric Annuli, and Parallel Plates

RICHARD W. HANKS

Union Carbide Nuclear Company, Oak Ridge, Tennessee

Recently Ryan and Johnson (*1*) proposed a stability parameter for pipe flow. For Newtonian fluids they showed that this parameter Z is proportional to the critical Reynolds number ($D\bar{v}\rho/\mu$) and is given by the relation

$$Z = 2\sqrt{\frac{1}{27}}N_{Re_c} \qquad (1)$$

They also demonstrated the utility of Z as a stability parameter for the isothermal pipe flow of power-law non-Newtonian fluids.

Hanks and Christiansen (*2*) extended the range of applicability of Ryan and Johnson's parameter to include heated flow of similar fluids, showing the temperature invariance of Z. However one may readily show the geometry dependence of Z by attempting to calculate the critical Reynolds number as observed by Davies and White (*3*) for flow between parallel plates. In order to calculate the experimental value one must postulate that Z be different for the two geometries.

In the present paper a generalized stability parameter will be proposed which is independent of the geometry of the flow system, is proportional to the Reynolds number for Newtonian flow, and contains Ryan and Johnson's (*1*) results for pipe flows in general as a special case.

DEVELOPMENT OF THE PARAMETER

In attempting to formulate a stability criterion of general applicability one should keep in mind the physical nature of such a parameter. It should be proportional to the conventional Reynolds number (which is a characteristic stability parameter) for the special case of Newtonian flow. The Reynolds number may be interpreted (*4*) physically as the ratio of the magnitude of certain inertial forces to the magnitude of the viscous forces acting on a fluid element. Therefore one might expect the generalized parameter to involve a similar ratio of magnitudes of forces.

The equations which describe the motion of a fluid are (*4*) the equation of continuity

$$\operatorname{div}(\rho\mathbf{v}) = -\frac{\partial\rho}{\partial t} \qquad (2)$$

and the equations of motion

$$\underset{(a)}{\rho\frac{\partial\mathbf{v}}{\partial t}} + \underset{(b)}{\frac{1}{2}\rho\,\mathbf{grad}(\mathbf{v}\cdot\mathbf{v})} - \underset{(c)}{\rho\mathbf{v}\times\zeta} = \underset{(c)}{\mathbf{F}} - \underset{(d)}{\mathbf{grad}\,p} - \underset{(d)}{\operatorname{div}\tau} \qquad (3)$$

The left-hand terms in Equations (3) represent the mass times acceleration of a fluid element, term (a) being the gradient of the translational kinetic energy of the fluid and term (b) arising from the vorticity of the flow. Terms (*c*) represent the forces due to the pressure and external force fields acting on the fluid, and term (d) represents the viscous forces.

It is suggested that when the magnitude of the acceleration force (b) reaches a certain multiple of the magnitude of the viscous force (d), the fluid motion will be unstable to certain types of disturbances and stable laminar flow will no longer exist. Mathematically this suggestion may be expressed as

$$|\rho\mathbf{v}\times\zeta| = K\,|\operatorname{div}\tau| \qquad (4)$$

At this point some rather general properties of the stability parameter K may be pointed out. From the nature of its definition K is a local parameter and therefore a function of position in the flow field. It is inherently a positive number. The term $\mathbf{v}\times\zeta$ vanishes at all solid boundaries and along the lines of symmetry of the velocity profile, whereas div τ does not. Therefore it follows that K must also vanish on solid boundaries and along the lines of symmetry of the velocity field. Hence $K \geqq 0$ everywhere, and at some point in the flow region K acquires a maximum value which shall be designated by the symbol $\overline{K}$.

It will be shown below, for Newtonian flows, that $\overline{K}$ is proportional to