

# Review

## Some fundamental analogies between solid, molten and aqueous materials: application of the concepts of energy levels and the band theory of solids

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An interaction of electrochemical ideas with the approaches of solid state physics provides some interesting analogies and themes in which certain aspects of electrolyte solutions, solid semiconductors and ionic liquids can be discussed in a somewhat inter-related manner. Some of the fundamental properties of this wide range of materials (solid semiconductors, molten salts or aqueous (electrolyte) solutions) may be unified into a loose theme derived from the general notions of the band theory of solids and its analogue in electrolyte solutions, namely, the electron and proton levels of electrolytes. The concepts which would describe the intermeshing behaviour of these materials will be derived from: the band theory of semi-conductors; Gurney's ideas on the occupied and vacant proton levels in electrolyte solutions; Rose's approach to the electron energy levels in solids and electrolytes; Fuller's views on the conceptual analogies between semi-conductors and electrolyte solutions; interpretation of molten salts put forward by Bockris and co-workers; and, finally, the *industrial* applications of Gurney's ideas made by Vermilyea in his interpretations of the corrosion of aluminium in water and the effect of various inhibitors on this corrosion reaction.

### 1. Introduction

The object of this review is to interweave approaches based on electrochemistry and solid state physics in a manner that brings out some basic analogies between aspects of the behaviour of electrolyte solutions, semiconducting solids and molten salts.

Modern electrochemistry is usually regarded as consisting of two main branches termed [1] *electrodics* and *ionics*, the former dealing with phenomena in the solid-electrolyte interphases and the latter concerned with the structure and properties of the electrolyte solutions. That solid-state concepts should prove of some value in elucidating the nature of processes that occur across *solid*-electrolyte interfaces is obvious enough and supported in details by the contents of a recent monograph [2]. What does merit some explanatory comments, however, is the attempt to discuss, within the present article, some

aspects of the physical chemistry of electrolyte solutions in relation to the solid-state concepts. There are a few matters associated with the elucidation of nature of electrolyte solutions which appear to lend themselves to much better conceptual insights if one draws *analogies* between the features of the electrolyte solutions and the solid-state phenomena. For example, corresponding to the energy levels of atoms and energy bands of solids are Gurney's [3] assignments of *proton levels* to various electrolyte solutions, both in aqueous and non-aqueous media. The concept of proton levels [3] in electrolyte solutions, which parallels the concept of levels and bands in solids, is not only a useful device to represent graphically the various aspects of proton equilibria in solutions but also affords a unique procedure for interpreting vital data of industrial interest [4]. Very significant extensions of Gurney's concepts have also been

made by Gerischer [5] in relation to redox reactions on electrodes, and variations of these ideas have been applied by others [6, 7] to a variety of general electrochemical problems.

Attempts have also been made in the literature on solid-state physics [9, 10] to delineate the comparative significance of energy levels in solids and electrolytes since an understanding of this problem provides useful guidelines in the choice of "electrode contacts" to solids for a variety of technological and laboratory applications. Also of interest in connection with an approach of this kind [9, 10] are the inter-relationships between lattice energies, heats of hydration and heats of solution, reviewed by Conway and Bockris [11], and the empirical correlations between band gaps and heats of hydration [9, 10]. An important aspect of the exercise of this type [9, 10], as stated by Rose [10], is to introduce some chemical intuitive understanding of the cohesive forces in solids, both before and after their dissociation into an electrolyte solution, into discussions heavily oriented towards Madelung-type of calculation based on Born's electrostatic model.

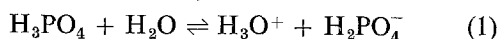
Another suitable subject in the present context is the examination of very interesting analogies that have been shown to exist [12] between the behaviour of water and that of a typical semiconductor such as silicon [12-14]. For example, the electron-hole equilibrium in silicon shows features similar to those exhibited by the ionic equilibrium of water.

The activation energies for the viscous flow and ionic transport in molten ionic salts have been shown by Emi and Bockris [15] to be semi-empirically related to the melting points,  $T_m$ , of the corresponding salts. Since transport phenomena in molten salts and related matters are an integral part of the behaviour of electrolytes and appear to be related to a quantity,  $T_m$ , which is diagnostic of the solid-state cohesion in solids, this work [15] will also be briefly mentioned here.

## 2. Gurney's concept of occupied and vacant proton levels in electrolyte solutions

Gurney [3] examined a great deal of data available on proton transfer reactions in solutions in an attempt to systematize the discussion of energetics of proton transfer reactions, following earlier classification of these reactions into various distinct types by Wynne-Jones [16].

He defined a quantity  $J$ , as the work required to carry out a proton transfer in a solvent. For a typical case of proton transfer from  $\text{H}_3\text{PO}_4$  to  $\text{H}_2\text{O}$  in solvent water,



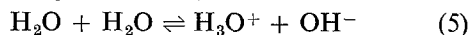
Gurney deduced that the quantity  $J$  is given by,

$$J = kT \ln K_x \quad (2)$$

where  $K_x$  is related to  $K$ , the auto-protolysis constant of phosphoric acid, which is



The relationship between  $K_x$  and  $K$  is given by  $-kT \ln K_x = -2.303 kT \log K - \log(55.51)$  (4) where the factor 55.51 refers to the fact that the basic quantity of the solvent water chosen is 1000 g which is equivalent to 55.5 moles of water. Thus for the example chosen, i.e., phosphoric acid, the value of  $K$  at  $0^\circ\text{C}$  is  $8.983 \times 10^{-3}$  and the value of  $J$  obtained is 0.2056 eV. Similarly, for carbonic acid the data of Gurney lists the value of  $K = 2.36 \times 10^{-11}$ , from which calculation of  $J$  by means of Equations 2 and 4 gives  $J = 0.6708$  eV in this case. When considering the auto-protolysis of water, i.e.



Gurney showed that the relationship between  $K_x$  and  $K$  will be different and will now be given by

$$\ln K_x = \ln K - 2 \ln M \quad (6)$$

where  $M$  represents the number of moles of solvent contained in the basic quantity of solvent (i.e. 1000 g) chosen here, after Gurney [3], i.e. 55.51. With the value of  $K$  for water, i.e.  $K_w$ , the auto-protolysis constant, taken as  $1.362 \times 10^{-14}$  at  $60^\circ\text{C}$ , he obtained  $J = 1.092$  eV. In other words, the work required to transfer a proton from one molecule of water to another, in pure water at  $60^\circ\text{C}$ , was estimated [3] to be 1.092 eV ( $\approx 25$  kcal). By similar evaluation of values of  $J$  for a number of proton transfers, Gurney was able to construct proton level diagrams which represented the  $J$  values for various proton transfers, arranged vertically in order of magnitude, and referring to  $J$  values in a given solvent, e.g. water, methanol, formic acid, etc. For example, in a proton level diagram in water, the  $J$  values will correspond to proton transfers such as the one represented in Equation 1.

An important point to mention in connection with the present discussion is that one can speak of occupied proton levels (e.g.,  $\text{H}_3\text{O}^+$ ) and

vacant proton levels (e.g.  $\text{H}_2\text{O}$ ). Also, obviously, even though  $\text{H}_2\text{O}$  is a vacant proton level with respect to  $\text{H}_3\text{O}^+$ , it is an occupied proton level as compared to  $\text{OH}^-$ . Similarly,  $\text{H}_2\text{PO}_4^-$  is an occupied proton level in comparison to  $\text{HPO}_4^{2-}$  whereas it is a vacant proton level with respect to  $\text{H}_3\text{PO}_4$ . The designation of these occupied and vacant levels thus extends further the analogy to the solid-state concepts and is presumably based on earlier work of Gurney [17] in which he assigned energy levels to electrolyte components in much the same way as solids are extended treatments in terms of electron levels. The latter work, of course, has since been much extended by Gerischer and co-workers in their discussions of electron transfer reactions on semiconductors [5].

In order to obtain clear terminology of occupied and vacant proton levels, it is helpful to consider some examples further. In a reaction such as in Equation 1, which is representative of most of the proton transfer reactions involving weak acids and bases as far as the present argument is concerned, the  $J$  values calculated refer to a process in which the proton is *raised* from a lower occupied proton level (e.g. as in  $\text{H}_3\text{PO}_4$ ) of a species to the vacant proton level of an  $\text{H}_2\text{O}$  molecule. The  $J$  values thus calculated specify the magnitude by which the initially occupied level (e.g.  $\text{H}_3\text{PO}_4$ ) is *below* the vacant level of  $\text{H}_2\text{O}$ . On the basis of this, one can obviously arrange the  $J$  values in a vertical order in which the magnitude of separation from the level of  $\text{H}_2\text{O}$  is a measure of the extent to which the initially occupied level of the molecule such as  $\text{H}_3\text{PO}_4$  lies below the vacant level of  $\text{H}_2\text{O}$ , as has been done, after Gurney [3], on the right hand side (labelled "vacant proton levels" – see below for elaboration) of the proton level diagram shown in Fig. 1. It may be noted that in this drawing (Fig. 1, right hand side), the vacant level of  $\text{H}_2\text{O}$  falls just over 1 eV (at  $25^\circ\text{C}$ ), assuming, as an arbitrary reference, the vacant proton level of  $\text{OH}^-$  as zero (this value of  $\sim 1.03$  eV for  $\text{H}_2\text{O}$  at  $25^\circ\text{C}$  arises, of course, from Equations 2 and 6), the other levels being referred to this scale.

In the auto-protolysis of water (i.e. Equation 5), "the proton is raised to the vacant level of one  $\text{H}_2\text{O}$  molecule from the occupied level of another (distant)  $\text{H}_2\text{O}$  molecule" [3], and the value of  $J$  associated with such a transfer is  $\sim 1.03$  eV at  $25^\circ\text{C}$ , as stated earlier. This would yield then two scales of expressing the proton

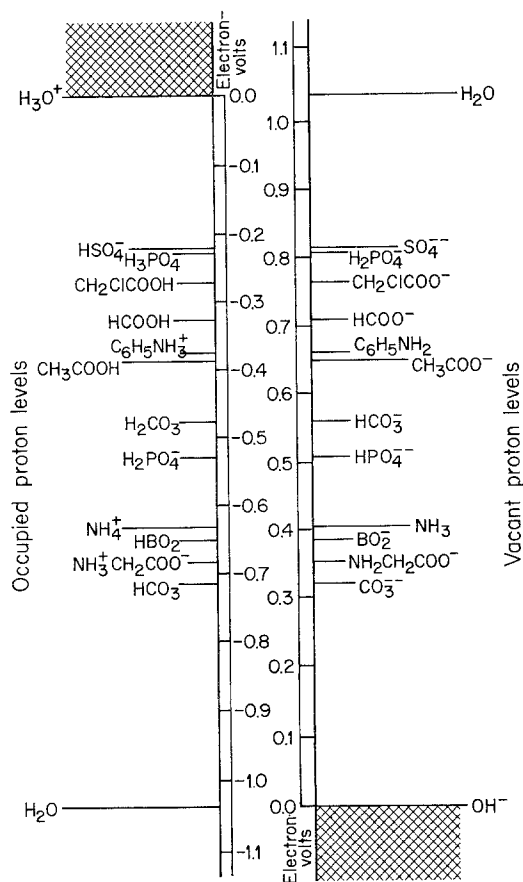


Figure 1 The proton level diagram, after Gurney [3]. The  $J$  values (see text for explanation) are in water at  $25^\circ\text{C}$ .

levels of molecules and ions in aqueous media, one in which the *vacant* level of  $\text{H}_2\text{O}$  is taken as 1.03 eV (with the vacant proton level of  $\text{OH}^-$  zero as stated earlier) and the other in which the *occupied* level of  $\text{H}_2\text{O}$  (i.e.  $\text{H}_3\text{O}^+$ ) is taken as zero. The proton levels expressed on the latter scale are shown in the left hand side (labelled "occupied proton levels") although it is obvious that conceptually there is no difference in the two ways of expressing these proton levels (Fig. 1).

Another feature of this representation (Fig. 1) merits comment. When a proton has been added to an  $\text{H}_2\text{O}$  molecule, it becomes an  $\text{H}_3\text{O}^+$  ion; so when one speaks about the energy of the occupied proton level of  $\text{H}_3\text{O}^+$ , one is merely referring, by a different name, to the energy of the vacant proton level of the neutral  $\text{H}_2\text{O}$  molecule. Similarly, except for the name, the occupied proton level of the  $\text{HCO}_3^-$  ion would be energetically equivalent to the vacant proton

level of the  $\text{CO}_3^{2-}$  ion. This point has been indicated in Fig. 1 and has been discussed in detail by Gurney [3].

Proton level diagrams of the type depicted in Fig. 1, and related concepts, in addition to their use in the interpretation of data [4] vital to applied electrochemistry (see below), are also of great scientific and pedagogic value in the analysis of some fundamental aspects of electrolyte solutions. One may consider, for example, the dissociation of strong acids in aqueous media in terms of such diagrams. For the strong acids, the dissociation is essentially complete not only in very dilute solutions but also in moderately concentrated solutions. In terms of Gurney's concepts when a distant  $\text{H}_3\text{O}^+$  ion has been formed by a proton transfer from the strong acid molecule to a neutral  $\text{H}_2\text{O}$ , a certain amount of work would be required to raise a proton from the  $\text{H}_3\text{O}^+$  ion to the vacant proton level in the distant anion. In the proton level diagram appropriate to this situation, the occupied proton levels of strong acid molecules such as  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and  $\text{HClO}_4$  in aqueous solutions must lie *above* the level of  $\text{H}_3\text{O}^+$  ion whereas the vacant proton levels of the corresponding anions ( $\text{HSO}_4^-$ ,  $\text{Cl}^-$  and  $\text{ClO}_4^-$ ) will lie an equal distance *above* the vacant proton level of neutral  $\text{H}_2\text{O}$  molecule. This has been schematically presented, after Gurney [3], in Fig. 2 for the case of  $\text{HCl}$ ; this figure also includes some interesting details on a typically weak acid, the  $\text{CH}_3\text{COOH}$ . If sodium acetate is added to the

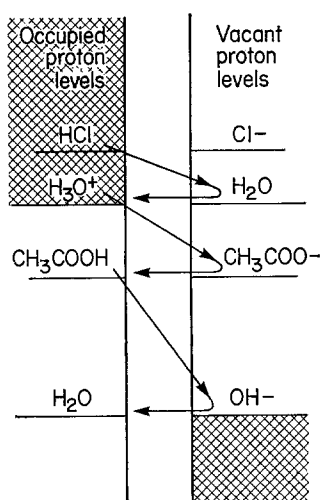


Figure 2 A schematic representation of occupied and vacant proton levels in some aqueous acidic solutions, after Gurney [3].

$\text{H}_3\text{O}^+$  to form neutral  $\text{CH}_3\text{COOH}$ , a situation also presented in Fig. 2. In contrast to the strong acids, the occupied proton level of a typically weak acid such as  $\text{CH}_3\text{COOH}$  lies *below* the occupied proton level of  $\text{H}_3\text{O}^+$  whereas the vacant proton level of the  $\text{CH}_3\text{COO}^-$  ion lies an equal distant *below* vacant proton level of the neutral  $\text{H}_2\text{O}$  mole (Fig. 2).

The fact that  $\text{HNO}_3$  is not completely dissociated follows from the calculated value of  $J$  as outlined above. For example, Gurney has estimated that the  $J$  value for the transfer of a proton from  $\text{HNO}_3$  to  $\text{H}_2\text{O}$  is *positive* at  $25^\circ\text{C}$  and equal to 0.052 eV. In terms of the proton level diagrams  $\text{HNO}_3$  will, therefore, be in a situation very similar, qualitatively, to that of  $\text{CH}_3\text{COOH}$ , i.e.  $\text{HNO}_3$  below  $\text{H}_3\text{O}^+$  and  $\text{NO}_3^-$  below  $\text{H}_2\text{O}$ , as has been shown [3] in Fig. 3, in which some other moderately weak acids are also included. The interpretation of this diagram (Fig. 3) follows rather obviously from the foregoing discussion here. These proton level diagrams for certain cases of non-aqueous solvents such as methanol, ammonia and formic acid have also been examined by Gurney [3].

Some extensions of Gurney's concept of occupied and vacant levels in electrolytes have been discussed by Reilley [6], who has given free energy levels, both for protons and electrons, for several electrolytes. The basic principles involved in this representation are very similar to those of Gurney [3] although detailed definition of some quantities is somewhat different and may be presented, after Reilley as follows.

In the proposed proton free energy scale, the levels are expressed either in units of electron solution of  $\text{HCl}$ ,  $\text{CH}_3\text{COO}^-$  will combine with

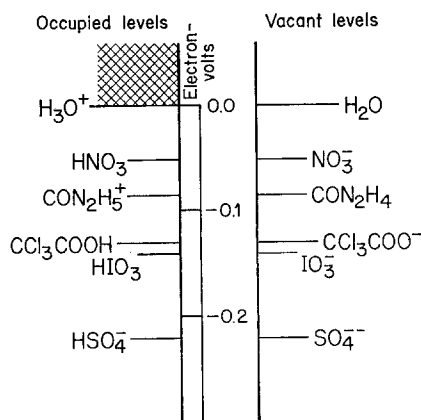


Figure 3 The occupied and vacant proton levels for some acids, after Gurney [3].

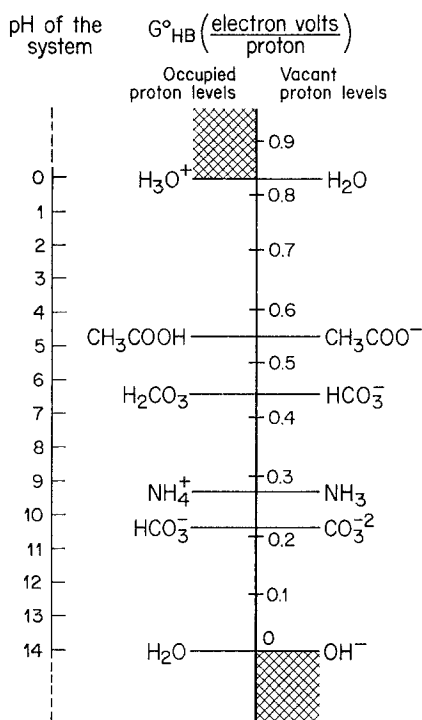
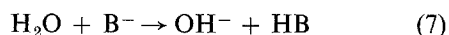


Figure 4 The proton free energy levels for the shown substances as presented by Reilley [6]. The standard free energy level of the  $\text{H}_2\text{O}$ ,  $\text{OH}^-$  system has been taken, arbitrarily, as zero.

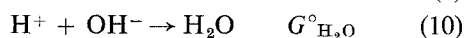
volts per proton ( $G^\circ$ ) or as pH. In such a scale, the pH is an index of the *average* proton free energy per proton and is determined by the energy values (i.e.  $G^\circ$  values) of the levels present as well as by the *relative population* of these levels. The  $G^\circ$  values in such a scale (Fig. 4) are deduced as follows. For a proton transfer reaction such as



in which B denotes a base, the free energy change,  $\Delta G_n^\circ$  is given by

$$\Delta G_n^\circ = -kT \ln \frac{K_w}{K_a} \quad (8)$$

where  $K_w$  is the auto-protolysis constant of water,  $K_a$  is the dissociation constant of the acid HB; the units of  $\Delta G_n^\circ$  are eV per proton and  $k$  is  $8.615 \times 10^{-5}$  eV per degree-proton. The  $\Delta G_n^\circ$  change in Equation 7 refers to the energy difference between the reactions



such that

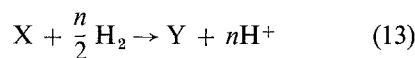
$$G_{\text{HB}}^\circ - G_{\text{H}_2\text{O}}^\circ = \Delta G_n^\circ. \quad (11)$$

By choosing arbitrarily a zero value for  $G_{\text{H}_2\text{O}}^\circ$ , a scale of relative proton free energies may be established and is given, at  $25^\circ\text{C}$ , by

$$G_{\text{HB}}^\circ = -0.059 \log \frac{K_w}{K_a}. \quad (12)$$

In the above representation, water is assumed to have unit concentration and the standard state of the solutes is in  $\text{mol litre}^{-1}$ . A proton free energy diagram based on these considerations and taken from Reilley [6] is shown in Fig. 4 along with the corresponding pH values. Although the proton free energy level diagrams (Fig. 4) are similar in general principles and significance to the "J" value representation of Gurney (Figs. 1 to 3), the detailed interpretations involve some additional matters which have been discussed by Reilley [6].

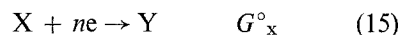
Similar to the *proton* free energy levels diagrams, one may also construct *electron* free energy levels diagrams. The free energy change,  $\Delta G_{\text{elec}}^\circ$ , in the electron transfer reaction such as



is given by

$$\begin{aligned} \Delta G_{\text{elec}}^\circ &= -kT \ln K = kT \ln \frac{[\text{X}]}{[\text{Y}][\text{e}]^n} \\ &\quad - kT \ln \frac{[\text{H}^+][\text{e}]}{[\text{H}_2]^{\frac{1}{2}}} \end{aligned} \quad (14)$$

where  $K$  represents the equilibrium constant for the electron transfer reaction, in Equation 13. The  $\Delta G_{\text{elec}}^\circ$  value is given by the free energy difference between the reactions



such that

$$\Delta G_{\text{elec}}^\circ = G_{\text{X}}^\circ - G_{\text{H}}^\circ. \quad (17)$$

By assuming arbitrarily that

$$G_{\text{H}}^\circ = -kT \ln \frac{[\text{H}_2]^{\frac{1}{2}}}{[\text{H}^+][\text{e}]} = 0. \quad (18)$$

One may establish a scale of relative electron free energies. This scale at  $25^\circ\text{C}$  is given by

$$G_{\text{X}}^\circ = -kT \ln \frac{[\text{X}]}{[\text{Y}][\text{e}]^n} = -kT \ln K. \quad (19)$$

Here again, it is assumed that water has unit concentration and that the standard state of the solutes is expressed in  $\text{mol litre}^{-1}$ ; the gases, of

course, will be expressed in atmosphere. If one rearranges Equation 19 as

$$-kT \ln e = \frac{kT}{n} \ln K - \frac{kT}{n} \ln \frac{[Y]}{[X]} \quad (20)$$

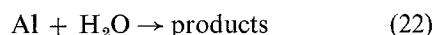
and, hence, as

$$E_e = E^\circ_x - \frac{kT}{n} \ln \frac{[Y]}{[X]} \quad (21)$$

where  $-nE^\circ_x = G^\circ_1$ , one obtains a form of Nernst equation, i.e. Equation 21. Hence the electron free energy scale (i.e. Equation 19) may be related to the corresponding potential (i.e. Equation 21) associated with the electron transfer reaction such as Equation 13. The potential,  $E_e$ , is an index of the *average* electron free energy per electron of an assembly of unoccupied and occupied electron free energy levels and is determined by the energy values of the levels present as well as by their relative population; i.e.  $E_e$  has the same significance for the electron free energy diagram (Fig. 5) as pH has for the proton free energy level diagram (Fig. 4). When in the case of a simple redox pair, both the oxidized and the reduced species are in their standard state, the population of occupied and

unoccupied levels in the system is equal, i.e.,  $[X] = [Y]$  in Equation 13 and thence  $E_e = E^\circ_x$  in Equation 21. In this connection one may mention the assignment of occupied and unoccupied levels to redox electrolytes by Gerischer in his formulations of equations for the rate of a redox electrode reaction on a semi-conducting surface [5]. In Fig. 5, an electron free-energy levels diagram, along with the corresponding  $E_e$  values, has been presented after Reilley [6]. The general interest of such diagrams (Figs. 4 and 5) lies in their value in predicting and illustrating the relative reaction tendency of some electrochemical and chemical systems under certain conditions; some of these cases have been discussed by Reilley [6]. The point of interest in the present discussion is, again, the fact that such representations provide very useful *analogies*, e.g. *in terms of occupied and unoccupied energy levels between electrolyte solutions and solids*. Also transitions between various levels in electrolytes, as explained in the discussion of Figs. 1 to 3 are quite similar to the interband transitions in semiconductors in that "energy gaps" have to be negotiated.

A very interesting recent application of Gurney's ideas to the industrially important problem of the inhibition of the corrosion reaction,



has been carried out by Vermilyea and Vedder [4]. They have examined the effects of a very large number of potential and possible inhibitors on the rate of reaction given in Equation 22. The products of this reaction are complicated in the sense of being a mixture of amorphous oxide, hydroxide and the dissolution products (precipitated or occluded within the oxide) of the oxide and hydroxide, the exact composition of the dissolution products depending on the composition, pH and ionic strength, etc. of the electrolyte.

It was observed that some aspects of the inhibition of this reaction by various substances in the electrolyte can be interpreted on the basis of the plot shown in Fig. 6. The proton level  $J$ , was obtained by combining Gurney's Equations 2 and 4 here into the abbreviated form

$$-J = 0.059 (1.744 - \log K) \quad (23)$$

where  $K$  is the appropriate dissociation constant of the acidic inhibitor such as  $\text{H}_2\text{WO}_4$ ,  $\text{H}_3\text{AsO}_4^-$ ,  $\text{H}_2\text{SeO}_4$  etc. The choice of the suitable acidic dissociation constant (e.g. whether first, second

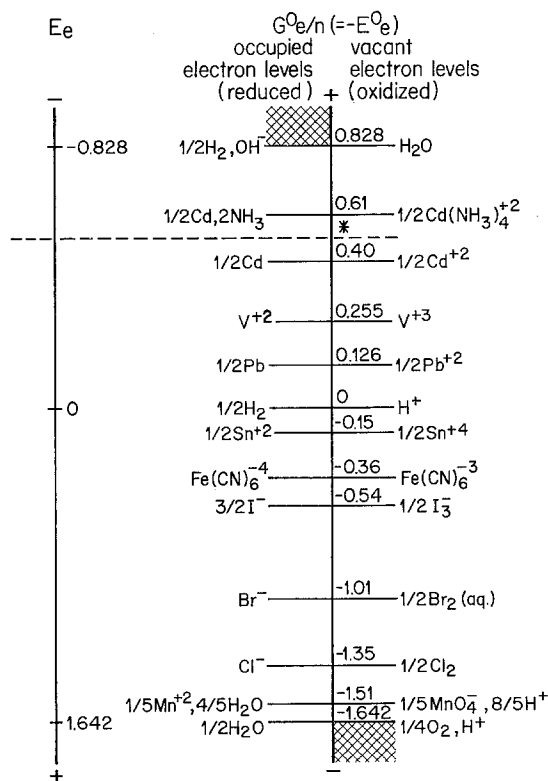


Figure 5 Electron free-energy levels diagram, as presented by Reilley [6].

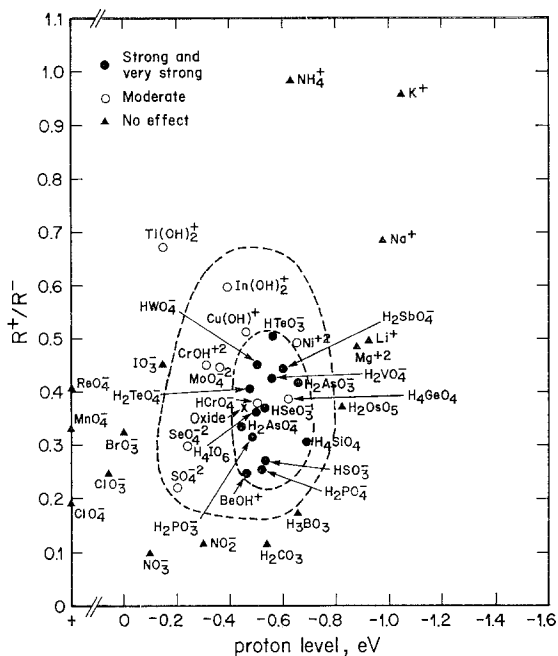
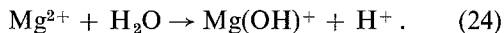


Figure 6 Correlation of inhibitor effectiveness for the (aluminium + water  $\rightarrow$  P) reaction with proton level, and, ratio of radius of positive ion in the inhibitor to the radius of negative ion. After Vermilyea and Vedder [4].

or third, etc. dissociation is appropriate when multiple dissociations are possible) was dictated by the ionization that would be likely at pH 5, the latter being chosen as the reference pH for the comparison of the effectiveness of various inhibitors. For the simple cationic inhibitors such as  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$  etc. the  $J$  values referred to the proton transfer reaction such as



In Fig. 6, the  $R^+/R^-$  ratio denotes the ratio of the radius of the cation (e.g. W in  $\text{HWO}_4^-$ ) in the inhibitor to the radius of the oxygen ion. The interpretation of Fig. 6 is that for an inhibitor to be very effective its  $J$  level should be close to the estimated  $J$  level of the (solid) aluminium surface (under conditions of the inhibition experiment, of course); the  $J$  levels of strong and very strong inhibitors fall between  $-0.44$  and  $-0.69$  eV and may be compared to the estimated  $J$  value of the surface which is  $-0.45$  eV. It was suggested that [4] this requirement arises from the fact that hydrogen bonding between the inhibitor, which is strongly bound to the surface as multilayered surface compound, and the surface is essential in order for the inhibitor to impart very strong protection to the surface. Such hydrogen bonding is possible, of course, if the  $J$  value of the

inhibitor is close to the  $J$  value of the surface such that facile proton exchange can take place. Otherwise, a large difference between the inhibitor  $J$  value and that of the surface, can lead to a large "forbidden gap" for the proton transfer reaction thus prohibiting hydrogen bonding to the surface and thereby failing to create conditions concluded [4] as favourable to maximum inhibitor effectiveness. For complete interpretation of Fig. 6, the role of  $R^+/R^-$  value should also be indicated, although it has no bearing on the discussion of occupied and unoccupied levels in electrolytes. The strong and very strong inhibition in Fig. 6 is heralded by substances for which the  $R^+/R^-$  ratio is close to the  $R^+/R^-$  ratio of aluminium oxide. In other words if the cationic radius of the cation of the inhibitor is close to that of  $\text{Al}^{3+}$ , strong inhibition will result. Vermilyea and Vedder [4] regard this fact as indicating that an effective inhibitor "must fit the structure of aluminium oxide" [4]. This fact appears, however, to lend itself to some further extension on the lines of Vermilyea and Vedder [4]. Equal or nearly equal,  $R^+/R^-$  ratios would show roughly comparable magnitudes of lattice energies, and, hence lack of strong electrostatic polarization at the interface between the inhibitor and the aluminium oxide. Very low  $R^+/R^-$  values of the inhibitor can give rise to strong electrostatic fields in the interphase between the inhibitor and the oxide which can cause ionic conduction and hence lack of protection. Very high  $R^+/R^-$  values of the inhibitor would indicate low lattice energy and poor solid-state cohesion with the result that the lattice of the surface layer of the inhibitor would have a tendency to undergo ready collapse, with the consequent lack of protection again. Qualitative predictions on these lines in terms of solid-state cohesion of the surface layer in general [18, 19] and lattice energies [19], bond energies [18] and melting points (which are an index of the lattice energy for highly ionic compounds) in particular have been shown previously to lead to useful interpretations of some dissolution phenomena [18, 19].

It may be pointed out that strong inhibition suggested both by optimum (between  $-0.44$  and  $-0.69$  eV)  $J$  value and optimum  $R^+/R^-$  value (between 0.25 and 0.45) in Fig. 6 must be regarded as separate facts; any inter-relationship between these two facts, which tends to be suggested by Fig. 6 in which both the optimum  $R^+/R^-$  values and the  $J$  values are crowded in the

same sector of the drawing, must be regarded as purely incidental in the sense that the two do not depend on each other.

The paper of Vermilyea and Vedder [4] also includes several other interesting aspects of the retardation of Equation 22 by various inhibitors but a discussion of those matters is outside the scope of the present review. This work [4] must be regarded as an elegant attempt to systematize a very complex field which is much studied but little understood. It should be of great interest to extend the criteria of  $J$  values and  $R^+/R^-$  values suggested by these authors to other cases of corrosion-type reactions.

It may be added that the use of Gurney-type energy level diagrams in the interpretation of some aspects of electrolyte solutions has also been made by Nemethy and Scheraga [7] and Ruppel [9]. Recent excellent review by Conway [8] is recommended for some further specialized applications of these energy level diagrams in electrolyte solutions.

### 3. Electron energy levels in electrolytes and solids: Rose's approach

In his excellent monograph [10], and in his previous paper in collaboration with Ruppel and Gerittsen [9], Rose has made an unusual attempt in that he, a physicist, has presented the problem of cohesion in solids and the dissociation of ionic solids in water in terms other than purely Madelung-type descriptions. As he points out [10], to a physicist schooled in calculating the lattice energy by the Madelung procedure based on Born's electrostatic model, it is *at first* somewhat surprising that the heat of solution of an ionic solid should be a very small quantity as compared to the lattice energy. This is because the Madelung type of calculation refers to the electrostatic cohesive forces between closely placed ions of opposite charge within the crystal lattice and the dissolution of an ionic compound, e.g. in water, presumably destroys all these forces with the resultant separation into individual ions placed (at least in dilute solution) quite far apart from each other – hence one should expect a high heat of solution. What is forgotten here, of course, is the fact of hydration of ions, which Rose is quick to point out to the solid-state physicists [10] and which is quite obvious to an electrochemist [11]. In fact, the various quantities under discussion are related [11] by the equation

$$\Delta H_{s.p.} = -U + \Delta H_{s+} + \Delta H_{s-} \quad (25)$$

where  $\Delta H_{s.p.}$  is the heat of solution of the ionic solid;  $U$  is the lattice energy per mole;  $\Delta H_{s+}$  is the heat of solvation (i.e. hydration if water is the solvent) of the cation;  $\Delta H_{s-}$  is the heat of solvation of the anion. For accurate estimates, the lattice energy  $U$  in Equation 25 should, in fact, refer to the corresponding heat content term [11] for the appropriate finite temperature and computed from the equation

$$U = U_0 + \int_0^T C_{p,salt} dT - \sum_{ions} \int_0^T C_{p,gas\ ions} dT \quad (26)$$

where  $C_p$  denotes heat capacity at constant pressure.

In any case, experimentally, it is observed that  $\Delta H_{s.p.}$  is usually a small fraction ( $< 5\%$ ) of  $U$  and the ions separated on dissociation of the solid lattice in a solvent, and thence the loss of  $U$ , are stabilized by undergoing solvation such that over  $\sim 95\%$  of  $U$  "lost" is "recovered" by the ions in the form of  $\Delta H_{s+}$  and  $\Delta H_{s-}$ . In terms of Rose's description [10], starting from ions in free space, the major gain in energy when these ions are assembled into a crystal lattice is the destruction of the Coulombic energies beyond an ionic radius. When these ions are introduced into a solvent, the major gain in energy is also the destruction of the same Coulombic energy by the dielectric constant of the solvent. This would imply that the energies of the ions in an ionic solid are roughly equivalent to the energies of ions in a solvent assuming that the heat of solution is small, the latter being valid at least for the dissolution of alkali halides in water (high dielectric constant). On the basis of this it has been suggested [9, 10] that the energy levels of electrons on ions in an electrolyte (made in a solvent of high dielectric constant such as water) are roughly equivalent to the same in an ionic crystal. *In other words approximately the same amount of work will be needed for transferring an electron from  $Cl^-$  to  $Na^+$  in a salt solution as in the crystal.* In this way, one may calculate the energies of electrons on *individual* ions in an electrolyte relative to vacuum and use these levels as rough guides to the energies of the electrons on ions in the solid and therefrom to the electronic behaviour of ionic solids and electrolytes in contact. From the heats of hydration, or solvation in general, one may thus construct an electronic energy level diagram in



which the energy of the electron on an individual ion (either in the crystal lattice or in the solution) is expressed relative to the vacuum and such an energy level diagram has been presented in Fig. 7 after Ruppel *et al.* [9]. For calculating the electronic energy level of, for example, negative chloride ion for such a diagram (Fig. 7), one notes that the electron on  $\text{Cl}^-$  in solution (and hence in the solid since heat of solution is ignored) is situated below vacuum by an energy equal to the sum of the heat of hydration of  $\text{Cl}^-$  and the electron affinity of Cl. The position of  $\text{Na}^+$ , similarly, in this diagram (Fig. 7) is given by the ionization potential of Na *minus* the heat of hydration of  $\text{Na}^+$ , since the energy thus obtained will give the magnitude by which the outer electron of a neutral sodium atom is below vacuum. In order to make clear why one has to resort to heats of hydration in order to obtain this kind of diagram for *solids*, it may be pointed out that heats of hydration, in a way, provide a means for calculating the "lattice energy" of the *individual ion* which cannot be determined by the Madelung-type procedure. In the electrostatic calculations of the physicists, one

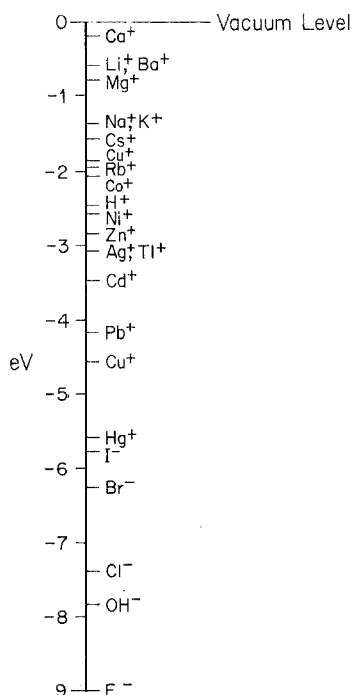


Figure 7 Electronic energy levels in solids derived from their heats of hydration on the basis of considerations put forward by Ruppel *et al.* [9] and discussed in the text here.

always deals with *ion pairs* for calculating the type of interactions being discussed here and no information is obtained on the individual ions; the latter information is, however, needed for a variety of situations of technological interest and, it seems that, is readily deduced by considerations of heats of hydration. As an example of use of this electronic energy level diagram in the considerations of solid materials and their properties, one notes that the position of  $\text{Na}^+$  in relation to vacuum may be regarded as a measure of the electron affinity (i.e. distance of conduction band to vacuum) of sodium compounds. Similarly, threshold for photo-emission from valence band to vacuum for compounds of chlorine is roughly indicated by the distance of  $\text{Cl}^-$  from the vacuum level. From the foregoing it follows that the difference between the levels of  $\text{Na}^+$  and  $\text{Cl}^-$  would be approximately equal to the band gap of NaCl. Similar conclusions may also be drawn, of course, for other combinations of cations and anions in Fig. 7. In fact, the forbidden gaps deduced from the energy level diagram such as Fig. 7, when plotted against the experimental band gap values for several ionic compounds, show a rather good correlation (Fig. 8). Thus the estimation of band gaps from Fig. 7 constructed on the basis of *heats of hydration* and related considerations yields values which are quite near the experimental  $E_g$  values (Fig. 8) as was first shown by Ruppel *et al.* [9] and subsequently discussed by Rose [10].

In the light of the foregoing discussion, it is interesting to comment, after Rose [10], on the well-known lack of solubility of the covalent

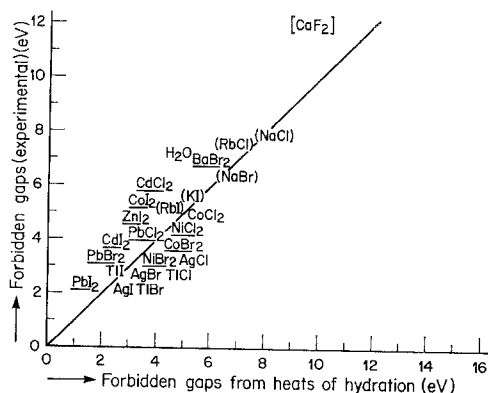


Figure 8 Plot of experimental values of band gaps of various inorganic compounds versus the band gap values estimated from the heats of hydration by Ruppel *et al.* [9].

compounds. A solid is either predominantly ionic or possesses a significant amount of (partial) covalent character. The "purely" ionic solid will dissolve in water with little evolution of heat since the energy of the ions in the solid and the electrolyte solution is roughly equivalent. When a solid possesses a (partial) covalent character, it must be deduced that covalence exists because the solid finds itself, by virtue of its covalence, in a lower or deeper energy state than it would have, were it "completely" ionic. If the covalent state represents a lower (or deeper) state than the ionic one, it must also be a lower state as compared to the ions in solution since the energy of ions in solution and in an ionic solid is roughly equivalent. It is obvious, therefore, that a covalent compound will have no tendency to undergo dissolution.

Certain other interesting aspects of Fig. 7 may be pointed out. The large electron affinities observed for the compounds of nickel, copper and silver etc., the small electron affinities of alkali and alkaline earth compound, and the large forbidden gaps of alkali halides follow from this electronic energy level diagram (Fig. 7). Another important conclusion from Fig. 7 is that halogens, with their deep lying energies as compared to vacuum, should make excellent blocking contacts (in the absence of specific chemical reactions) to the conduction bands of most solids [10], as indeed is observed in practice. In conclusion, it is noted that an electronic energy level diagram for individual ions in solids (Fig. 7), based on the considerations of heats of hydration, heats of solution and related quantities of the physical chemistry of electrolyte solutions, lends itself to a variety of interesting interpretations and deductions which are regarded as important to the understanding of solid state properties of materials [9, 10]. For further discussions of these matters, the reader is referred to the monograph of Rose [10].

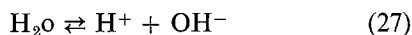
#### 4. Analogies between semiconductors and electrolyte solutions

It has been observed [12] that some interesting analogies exist between the properties and behaviour of a typical semiconductor, e.g. silicon and water. These analogies seem to provide penetrating conceptual insights into the nature and properties of semiconductors in terms readily appreciated by an electrochemist as well as a solid-state physicist. Furthermore, such analogies are great pedagogical aids in translating the

concepts and jargon of one field to the investigators in the other. A brief description of some of these analogies is presented here, after Fuller [12].

##### 4.1. Solvent properties of silicon and water

Pure silicon and pure water are both highly resistive materials, the specific resistance of silicon being about 1/106 that of pure water at 25°C. Like water, silicon may be regarded as a potential "solvent" medium, or more strictly a dielectric medium, within which motion and interaction of appropriate charged particles occurs. In water, the conduction is by ions whereas in silicon, conduction takes place by electrons and holes, the mobilities of the latter being about  $10^5$  to  $10^6$  times greater than those of the ions. Electrons and holes are, however, generally regarded [12, 20] to possess some attributes of the chemical species such as ions. The auto-protolysis of water may be represented as (cf. Equation 5)



although a more correct way to write Equation 27 is as in Equation 5, i.e. with  $\text{H}^+$  hydrated; this point is not of interest in present discussion, however, and Equation 27 may be taken to represent the situation. The auto-protolysis constant (or the ion-product constant),  $K_w$ , is given by the law of mass action as

$$[\text{H}]^+ [\text{OH}]^- = K_w \quad (28)$$

A determination of electrical conductivity at any temperature can yield  $K_w$  as follows. The electrical conductivity,  $\sigma$ , of  $\text{H}_2\text{O}$  is given by [12]

$$\sigma = N_i q (\mu_+ + \mu_-) \Omega^{-1} \text{cm}^{-1} \quad (29)$$

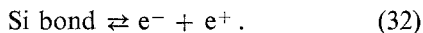
where  $N_i$  represents the number of ions per  $\text{cm}^3$ , of either sign;  $q$  is the charge on the electron;  $\mu_+$  and  $\mu_-$  denote the mobility of the  $\text{H}^+$  and  $\text{OH}^-$  ions, respectively in  $\text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$ . The values of  $\mu_+$  and  $\mu_-$  are obtained from dilution measurements on strong acids and bases,  $\sigma$  is known from the determination of electrical conductivity and  $q$  is, of course, known such that  $N_i$  can be determined from Equation 29. The  $N_i$  thus deduced is related (cf. Equation 27) to the  $K_w$  by

$$K_w = N_i^2 \quad (30)$$

so that  $K_w$  may be evaluated. The value of  $K_w$  at 25°C is equal to  $10^{-14}$  equivalents-litres<sup>-2</sup> or stated in terms of actual number of ions per  $\text{cm}^3$ ,

$$K_w = 3.6 \times 10^{27} \text{ cm}^{-6} \text{ at } 25^\circ \text{C}. \quad (31)$$

The relevance of the preceding discussion in the present context is that silicon may also be regarded to "ionize" in a manner very similar to the self-dissociation of water. The ionization of silicon to yield electrons and holes may be represented as



The electron thus released moves in the conduction band of silicon whereas the hole moves in the valence band. The self-dissociation in Equation 32 may also be represented, by application of the law of mass action, as

$$e^+ + e^- = K_{\text{Si}}. \quad (33)$$

By defining  $e^+ = e^- = n_i$ , one obtains

$$K_{\text{Si}} = n_i^2. \quad (34)$$

As for the determination of  $K_w$  for water,  $K_{\text{Si}}$  for silicon can be deduced from the electronic conductivity measurements on pure solid silicon. The conductivity  $\sigma$  for the present case may be written as

$$\sigma = n_i q(\mu_+ + \mu_-) \Omega^{-1} \text{ cm}^{-1} \quad (35)$$

or

$$n_i = \frac{\sigma}{q(\mu_+ + \mu_-)} \quad (36)$$

where  $q$  is the electronic charge ( $= 1.6 \times 10^{-19}$  C);  $\mu_+$  and  $\mu_-$  are, respectively, the mobility of the hole and electron, respectively, and are expressed in units of  $\text{cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ ;  $n_i$  is the number of carriers per  $\text{cm}^3$ . The values of  $\mu_+$  and  $\mu_-$  may be determined by a method due to Haynes and Shockley [21], since these quantities are not accessible by simple transport measurements as in the case of electrolyte solutions. The  $K_{\text{Si}}$  thus determined has a value at  $25^\circ \text{C}$  equal to  $10^{20} \text{ cm}^{-6}$ ; this  $K_{\text{Si}}$ , by analogy with  $K_w$ , may be regarded as the "ion product" (or more strictly the electron-hole product) for silicon.

The degrees of "ionization" of both water and silicon increase with increasing temperature. By examining  $K$  ( $= K_w = K_{\text{Si}}$  for the purposes of definition here) as a function of temperature and then using the integrated form of the Van't Hoff equation, which is

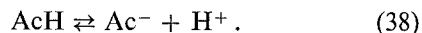
$$d \ln K = - \frac{\Delta H^\circ}{RT} + c \quad (37)$$

one may determine a heat of reaction,  $\Delta H^\circ$ , for the ionization of either water or silicon. This procedure must be regarded as approximate since

it fails to take into account any changes in the mobility of charge carriers with temperature and any departures from ideal behaviour. In any case the  $\Delta H^\circ$  value estimated from Equation 37 for water is 13.5 kcal whereas for Si its magnitude is 25.4 kcal, the latter being also the band gap value for silicon.

#### 4.2. Solute additions to water and silicon

If one regards both water and silicon as solvents, it should be possible to dissolve solutes in them, which is indeed observed. If acetic acid is added to water, it undergoes dissociation such as



The proton thus released in water makes it acidic. Similarly if an impurity such as boron is added to Si, it undergoes ionization such as



The hole thus introduced into Si by the ionization of boron renders it p-type. It is interesting, therefore, to regard p-type semiconductors as acidic solutions and n-type as alkaline solutions. The only major difference between the solute additions to the two solvents (i.e. water and silicon) is that the anion is mobile in water whereas the "anion" ( $\text{B}^-$ ) in silicon is immobile at ordinary temperatures, although significant mobilities of ions dissolved in solids can be achieved at high temperatures. Further details on this matter have been discussed by Fuller [12].

#### 4.3. Concentration cell and the p-n junction

If a concentration cell is set up between two electrolytes in separate compartments such that the only difference between the two electrolytes is their proton concentration, one may write the cell potential,  $E$ , as

$$E = \frac{RT}{F} \ln \frac{[\text{H}_2^+]}{[\text{H}_1^+]} \quad (40)$$

where  $[\text{H}_1^+]$  and  $[\text{H}_2^+]$  refer to the proton concentration in the first and the second compartment; here any non-ideality effects and liquid junction have been ignored. Since it has been seen that holes can be regarded as behaving as protons one may represent a p-n junction in a semiconductor as a concentration cell in holes. The potential across the p-n junction,  $E_{\text{pn}}$ , may thus be written as

$$E_{\text{pn}} = \frac{kT}{q} \ln \frac{[e^+]_p}{[e^+]_n} \quad (41)$$

where  $[e^+]_p$  and  $[e^+]_n$  represent, respectively, the

concentration of holes in the p and n “compartment” of the p–n junction; here, again, any non-ideality effects have been ignored. Fuller [12] has shown that quite satisfactory estimates of  $E_{pn}$  can be obtained by invoking analogies of the present type and thus using Equation 41.

For several further extensions of the essentials of the analogy between  $H_2O$  and Si outlined here, the reader is referred to the review by Fuller [12] and the papers by Reiss and co-workers [13, 20].

### 5. Aspects of ionic liquids: the $3.7R T_m$ rule of Bockris and co-workers

A case in which some rather interesting inter-lacing of the solid state and the physical chemistry of electrolytes occurs is afforded by ionic liquids, also termed synonymously, fused salts, molten salts or pure liquid electrolytes [22]. It is experimentally observed that, although the ionic liquids represent a fluid structure in which the solid crystal arrangement has been destroyed, the ions maintain the nearly same internuclear distance as in the solid state before melting. In fact, it is indicated that the ions are somewhat closer to each other in the fused salt than in the corresponding crystalline state. There is an increase in volume (between 10 and 25%), however, when a salt undergoes fusion and this increase in volume is believed to occur because of formation of holes (here a hole refers to an unoccupied volume of the ionic liquid caged between the ions and is thus quite different from the holes in the valence band of a semiconductor) so that the ionic liquid resembles Swiss cheese. This picture of the ionic liquid, called the hole model, was proposed by Furth [23] and has been extensively discussed by Bockris and co-workers [15, 22], although other suggestions regarding the structure of ionic liquids have also been put forward and reviewed recently by Bockris and Reddy [22]. The comparable magnitude of the interionic distance in the ionic liquid and the solid crystal suggests that short range order remains intact in the molten state. A profound consequence of this short range order in ionic liquids is that the band theory of *solids* can be applied also to these *molten* states, even though the bands tend to be somewhat diffuse [24].

The point of main interest in the present discussion, however, is the transport behaviour in the molten salt in relation to the solid state cohesion (as expressed in the melting point) of the corresponding crystal. As pointed out by Bockris and Reddy [22], all transport processes

in ionic liquids such as electrolytic conduction, diffusion and viscous flow basically involve similar events, i.e. “ionic movements and ionic drift in the preferred direction” [22], and must, therefore, be interrelated. It has, in fact, been observed that for the molten states the following relations are obeyed [15, 22]

$$E_\eta \simeq E_D \simeq 3.7 RT_m \quad (42)$$

where  $E_\eta$  is the experimental activation energy for the viscous flow,  $E_D$  is the activation energy for self-diffusion,  $T_m$  is the melting point on the Kelvin scale and  $R$  is the gas constant. The correlation between  $E_\eta$  and  $T_m$  is presented in Fig. 9, after Emi and Bockris [15]; the plot of  $E_D$  versus  $T_m$  has been shown in Fig. 10 and has been taken from Bockris and Reddy [22]. An index of solid state cohesion in crystals, i.e.  $T_m$  thus appears to be related to two fundamental properties of the corresponding molten state.

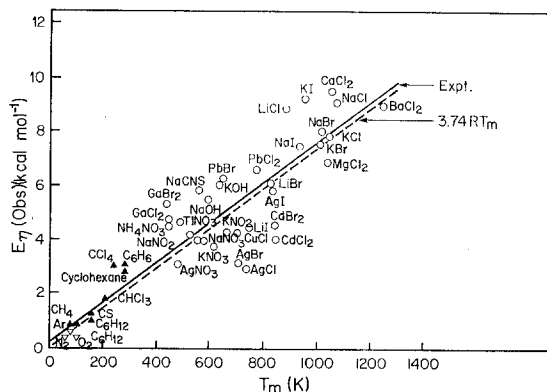


Figure 9 Correlation between the energy of activation for viscous flow and the temperature,  $T_m$  for the substances shown in the graph. Taken from Emi and Bockris [15].

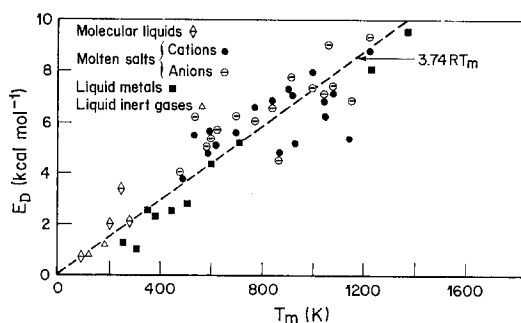


Figure 10 Correlation between experimental energy of activation for self-diffusion and the melting point,  $T_m$ , for various classes of substances. Taken from Bockris and Reddy [22].

Bockris and co-workers have put forward theoretical interpretations of these correlations (Figs. 9 and 10; Equation 42) by assuming the validity of the hole model for the molten states and then calculating the heat of activation of viscous flow and of self-diffusion on the basis of that model. In the mathematical formulations of the problem by Bockris and co-workers, the most recent version of which has been given by Emi and Bockris [15], an important step is the evaluation of a parameter termed,  $A$ , which is defined as the work done in transferring a mole of particles (i.e. ions in an ionic liquid but molecules in molecular liquids such as  $C_6H_{12}$ ,  $CH_4$  and  $O_2$  etc., also shown to obey the correlation in Fig. 9, for example) from the surrounding of a hole into its interior. In addition to the assumption of the general validity of the hole model, a further assumption is also made that "near or at the melting point, a hole is annihilated by the 'evaporation' into it of one particle; i.e., one particle just fills it" [22]. This latter assumption seems to be plausible in view of the rather elaborate justifications presented [15, 22]. The derivation of Emi and Bockris [15] of these correlations (Equation 42) is not given here since it does not bring out any new points of interest in the present discussion, which has been attempted only to indicate that magnitude of *solid state cohesion* as reflected in  $T_m$  appears to influence the transport properties of the corresponding ionic liquids.

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Received 1 February and accepted 2 April 1974.