



**J. A. YOUNG**

Auburn University  
Auburn, Alabama



**J. G. MALIK**

San Diego State College  
San Diego, California

# chemical queries

... especially for  
introductory chemistry teachers

## Question

What evidence, understandable by and acceptable to students, do most teachers cite to describe the transfer of charge from one electrode to another in the direct current electrolysis of an electrolyte solution?

## Answer

It is impractical to conduct a poll in order to answer this question reliably, but based on numerous informal conversations and reading of the pertinent literature, most teachers of beginning chemistry courses probably refer to factual evidence involving electrode processes.

The facts are these: We can indirectly count electrons which enter the solution and those which leave; in any given period of time, the numbers are equal. Further, in all direct current electrolyses, an observable change occurs at each electrode-solution interface. The change which is observed at the anode is always an oxidation, or another reaction which is the result of an oxidation. Similarly, the observed changes at the cathode-solution interface clearly suggest that a reduction reaction takes place in that region. Taken together, these facts imply the existence of a charge transfer process, through the medium of charged ions in solution.

One way this can occur would involve chemical reactions near each electrode. At the cathode, for example, positive or negative ions are reduced by the entering electrons:  $\text{Cu}^{2+}$  to  $\text{Cu}^+$ , or to  $\text{Cu}$ ;  $\text{MnO}_4^-$  to  $\text{MnO}_2$  (or to other oxidation states lower than +7, in the presence of hydronium ion). Or, the solvent might be reduced:  $\text{H}_2\text{O}$  to  $\text{H}_2$  and  $\text{OH}^-$ . Often, especially at high concentrations of solute and high current density, more than one reduction process might occur.

At the anode electrons are generated by oxidation: Common examples of such oxidation processes include the oxidation of the solvent:  $\text{H}_2\text{O}$  to  $\text{O}_2$  and  $\text{H}_3\text{O}^+$ ; the oxidation of ions:  $\text{Cl}^-$  to  $\text{Cl}_2$ ;  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ ; the oxidation of the electrode itself;  $\text{Ni}$  to  $\text{Ni}^{2+}$ . Again, more than one process may take place.

Additional evidence for the existence of ionic species in solution is often presented. The commonly cited examples for this include comparisons of differences in

the lowering of the freezing point of water by equally concentrated solutions of sugar and of salt, or other electrolytic solutes. Or, an examination of the conductivities of dilute and concentrated solutions of a weak electrolyte, such as acetic acid. Or, an examination of the colligative properties of an electrolyte dissolved in a solvent of low dielectric constant ( $\text{HCl}$  in toluene, for example) compared to the colligative properties of a similar solution, but using a solvent of higher dielectric constant ( $\text{HCl}$  in water). This evidence, indeed, says nothing about electrolytic processes, but it does support the postulate that ions are present only in those solutions which do "conduct" an electric current, and thus buttresses the details suggested above.

Introductory discussions often stop at this point. However, further exposition could point out that other events can be expected: For example, if  $\text{Cu}^{2+}$  is reduced at the cathode, the region near the cathode becomes negatively charged, due to the presence of spectator anions. These will tend to leave the cathode region at some average rate, and other positively charged cations will tend to enter the region, at some other average rate. The two rates will not ordinarily be the same. The anions, or cations, are surrounded by an environment of oppositely charged ions, and by molecules of solvent as well. These "drag" the moving ion, reducing its otherwise greater rate away from, or toward, the cathode as the case may be. We conclude that the effective movement of an ion might depend upon several factors: the magnitude of its charge, its size, the degree of solvation, and the concentration of counter-charged ions are the most important factors. In less simple electrolyte solutions, the possibility of complex ions should be included, such as  $\text{CuCl}_4^{2-}$  for the example mentioned; such ions will not only move in a different direction than solvated  $\text{Cu}^{2+}$  ions, they will move at a different rate.

To summarize, charge is transferred externally by electron flow, and internally by a variety of ion movements at different rates and directions, which depend upon the characteristics of each different ion that is present.

## Question

Why should gallium be a liquid near room temperature? Both indium and thallium are solids, and they are members of the same group.

We solicit questions for this column and reactions to the answers given. Correspondence should be addressed to Dr. Jim G. Malik at San Diego State College, San Diego, California 92115.

## Answer

Gallium, indium, and thallium have typical metallic properties. However, they all have rather low melting points for metals yet maintain typically high boiling points. Thus, the temperature range of the liquid state of these three metals is extraordinarily wide; gallium has the longest temperature range as a liquid of any known substance.

The boiling points of aluminum, gallium, indium, and thallium decrease regularly with increasing atomic size following the trend of their heats of sublimation (atomization). The melting points do not follow such a trend. As is the case with some other irregular trends, part of the explanation lies in the fact that these elements have different solid state structures. Hence the same process is not being compared when the melting of each is considered.

Aluminum and indium have face-centered cubic lattices and thallium has a hexagonal close-packed structure. Both of these structures are regular, tightly packed arrangements with a coordination number of 12, that is 12 nearest neighbors. Gallium has an irregular solid structure with seven non-equidistant neighbors. That is, the nearest atom has an interatomic distance of 2.44 Å, two others at 2.70 Å, two more at 2.73 Å, and two at 2.79 Å. The one short interatomic distance can be interpreted to indicate that metallic gallium consists of diatomic molecules. This conclusion is in accord with molecular orbital concepts.

Because of the rather large difference between the one shortest interatomic distance and the others, gallium can be said to have an "effective coordination number" of one, the same as is usually assigned to such well-defined molecules as H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and the halogens, all of which have low melting points. Thus it is not totally unexpected that gallium should melt readily at a low temperature. It is interesting to note that this rather open solid structure of gallium collapses to approximate a close-packed arrangement in the liquid state, accompanied by a considerable increase in electrical conductivity. Gallium is one of the few substances whose solid phase floats in its liquid phase.<sup>1</sup> The disruption of the solid configuration to the denser arrangement in the liquid state is consistent with the high boiling point of gallium.

## Question

In general, ions of transitional elements are stable when their *d* subshells are half-filled, completely filled, or completely empty. Then how do we account for the stability of chromium salts where Cr exists in the 3+ oxidation state, and also the stability of cobalt salts where Co is in the 2+ oxidation state?

## Answer

by Larry E. Bennett, San Diego State College, San Diego, California

The question is misleading since the first statement applies to gaseous ions, and the question itself implies

that these species have comparable stabilities in the combined state. Indeed, the Hund multiplicity rule correctly describes *gaseous ions* with half-filled subshells as more stable (other factors neglected) than gaseous ions whose partially filled subshells are not half-filled. But in considering the relative stabilities of the same ions as components of a compound, this uniquely identified stability may or may not play an important part, compared to other factors which influence stability.

For example, in their compounds, the *d*<sup>0</sup> Fe(VIII), *d*<sup>5</sup> Co(IV), *d*<sup>5</sup> Ni(V), and *d*<sup>5</sup> Cu(VI) species all satisfy the criteria mentioned but are quite unstable. On the other hand, *d*<sup>1</sup> Ti(III), *d*<sup>2</sup> V(III), *d*<sup>3</sup> V(II), *d*<sup>3</sup> Cr(III), *d*<sup>4</sup> Cr(II), *d*<sup>6</sup> Fe(II), *d*<sup>6</sup> Co(III), *d*<sup>7</sup> Co(II), *d*<sup>8</sup> Ni(II), and *d*<sup>9</sup> Cu(II) form stable compounds in spite of failing the criteria mentioned. Hence, there must be other criteria, with greater validity, to ascertain relative stabilities when these metal ions are combined and not in the gaseous state.

Indeed, stability is a thermodynamic term; it is directly related to free energy differences, and only indirectly to numbers of *d* electrons. The relation between stability and free energy differences can be generalized at the sacrifice of detail: In a non-gaseous system, the stability of an oxidation state for a metal ion will depend upon 1) the energy of its chemical interaction with its environment, 2) the ionization potential involved in its conversion to another oxidation state, and 3) the energy of the chemical interaction of the ion in that new oxidation state with its environment. A Born-Haber cycle could be constructed to illustrate these contributions in detail.

Or, the species mentioned in the question can be used to illustrate this point more broadly. Chromium(III) is usually stable relative to Cr(II), as the question has indicated. This is the result of a fairly *low* third ionization potential combined with a *large* stabilization of Cr(III), relative to Cr(II), through chemical interaction of the metal ions with their environments, the near-by ligands. With many ligands this couple receives an unusually large contribution to the overall stabilization from the large crystal field stabilization energy of Cr(III) (*t*<sub>2g</sub><sup>3</sup>) relative to Cr(II) (*t*<sub>2g</sub><sup>3</sup>*e*<sub>g</sub><sup>1</sup>). In oversimplified terms, ligands are more tightly bound to Cr(III) than to Cr(II).

In contrast, Co(II) is frequently found to be stable with respect to Co(III) as the result of a *high* third ionization potential relative to the chemical stabilization of Co(III) over Co(II). However, with certain ligands, such as ammonia and cyanide ion, the chemical stabilization becomes sufficiently large to make Co(III) the more stable oxidation state. The electronic configuration of Co(III) is (*t*<sub>2g</sub><sup>6</sup>) with this class of ligands. An unusually large difference in crystal field stabilization energies between Co(II) and Co(III) again partially contributes to the chemical stabilization, although other bonding energies are involved as well.

We hasten to mention that not all cases of oxidation state stability are determined primarily by crystal field stabilization energies and a careful analysis is required for each case. Fortunately a detailed treatment is available.<sup>2</sup> In this approach, the stability of gaseous ions with half-filled shells is energetically reflected in the ionization potential.

<sup>1</sup> For other similar substances, see "Chemical Queries," J. CHEM. EDUC., 45, 252 (1968).

<sup>2</sup> BUCKINGHAM, D. A., AND SARGESON, A. M., "Chelating Agents and Metal Chelates" (Editors: DWYER, F. P., AND MELLOR, D. P.), Academic Press, New York, 1964, p. 237.

## Question

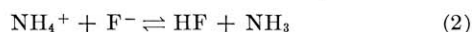
For the salt of a weak acid or the salt of a weak base, it is simple to derive the hydrolysis equilibrium constant,  $K_h = K_w/K_a$ , and from that relation to rearrange the terms to calculate the hydrogen ion concentration  $[H^+]$ . How does one derive the corresponding statement and find the hydrogen ion concentration for solutions of a salt of a weak acid and a weak base?

## Answer

To illustrate the derivation, the hydrolysis of  $NH_4F$ , the salt of the weak base, ammonia, and of the weak acid, hydrofluoric acid, will serve. However, it should be noted that not all chemists today prefer to use the word, hydrolysis, to identify this process. That is, from the Greek roots, hydrolysis should signify a breaking-up, with water as the agent which causes the phenomenon. Thus, in the equation as written here, it appears that water plays a part



Instead of considering water as an acid, above, the ammonium ion can be identified as the acid, thus



Equations (1) and (2) can be shown to be identical with respect to their chemical consequences, even though only eqn. (1) is properly described as a hydrolysis. There is no evidence known to us which conclusively demonstrates that ammonia in water is either in the form  $NH_3$  or  $NH_4OH$ . In the interest of simplicity, many chemists today prefer to use the symbol  $NH_3$ .

So, at least for the example chosen to illustrate the answer, it is not wrong to continue with eqn. (1). From this equation the expression for the equilibrium constant,  $K_h$ , can be written

$$K_h = \frac{[HF][NH_4OH]}{[NH_4^+][F^-]} \quad (3)$$

From eqn. (2)

$$K_h = \frac{[HF][NH_3]}{[NH_4^+][F^-]}$$

Either expression for  $K_h$  is an expression of the same number, the hydrolysis equilibrium constant. The numerator and denominator of the fraction in eqn. (3) are multiplied by both  $[H^+]$  and  $[OH^-]$ . (Since the hydrated proton is not exclusively present as  $H_3O^+$ , we choose to use  $H^+$  instead of the more cumbersome  $H(H_2O)_n^+$ .)

$$K_h = \frac{[HF] \times [NH_4OH] \times [H^+][OH^-]}{[H^+][F^-] \times [NH_4^+][OH^-]} \quad (4)$$

The terms separated by the otherwise unnecessary multiplication signs can be recognized as  $K_a$  for hydrofluoric acid,  $K_b$  for ammonia, and  $K_w$  for water. So eqn. (4) can be differently expressed

$$K_h = K_w/K_aK_b \quad (5)$$

The same result, eqn. (5), is obtained by multiplying the numerator and denominator of the expression obtained from eqn. (2) by both  $[H^+]$  and  $[OH^-]$ .

To obtain an expression for  $[H^+]$ , which does not appear in eqn. (5) [and cancels out in eqn. (4)], it is necessary to re-examine eqn. (1). That is, at all times, including in particular when equilibrium is established, the sum of the concentrations of oppositely charged species must be equal.

$$[NH_4^+] + [H^+] = [F^-] + [OH^-] \quad (6)$$

Further, in eqn. (1), the ammonium ion not present as such at equilibrium is therefore present as ammonium hydroxide (or ammonia). And, the fluoride ion not present at equilibrium is present as unionized acid. Since, initially, ammonium ion and fluoride ion were present in equal concentrations, we can write a mass balance expression.

$$[NH_4^+] + [NH_4OH] = [F^-] + [HF] \quad (7)$$

When eqn. (7) is subtracted from eqn. (6), a useful expression is obtained for the concentration of the hydrogen ion.

$$[H^+] - [NH_4OH] = [OH^-] - [HF] \quad (8)$$

If we had used eqn. (2) instead of eqn. (1), eqn. (8) would be as it is, now, except that  $[NH_3]$  would appear in place of  $[NH_4OH]$ .

Rearranging the expression for  $K_a$  and for  $K_b$  we obtain the final needed emphasis.

$$[HF] = \frac{[H^+][F^-]}{K_a} \quad [NH_4OH] = \frac{[NH_4^+][OH^-]}{K_b}$$

These terms are substituted into eqn. (8) in place of the terms  $[HF]$  and  $[NH_4OH]$ .

$$[H^+] - \frac{[NH_4^+][OH^-]}{K_b} = [OH^-] - \frac{[H^+][F^-]}{K_a} \quad (9)$$

A few more algebraic steps, including multiplying both sides of eqn. (9) by  $[H^+]$  and substituting  $K_w$  for  $[H^+][OH^-]$ , as well as rearranging the terms, permit this final result

$$[H^+] = \left( K_w \frac{K_aK_b + K_a[NH_4^+]}{K_aK_b + K_b[F^-]} \right)^{1/2} \quad (10)$$

In most cases, where solutions of 0.1 *M*, or higher, are involved, the concentrations of the cation and anion will be much greater in magnitude than the numerical value of  $K_a$  and  $K_b$ . In that event, eqn. (10) simplifies its appearance

$$[H^+] \cong \left( \frac{K_aK_w(NH_4^+)}{K_b[F^-]} \right)^{1/2} \quad (11)$$

For the cases where the concentration of the acidic cation, such as  $NH_4^+$ , is equal, or almost so, to the concentration of the basic anion, such as  $F^-$ , these terms cancel out of eqn. (11).

$$[H^+] \cong (K_aK_w/K_b)^{1/2} \quad (12)$$

Note that for the unique case where the acid and base from which the salt was derived are equally weak,  $K_a = K_b$ , eqn. (12) predicts that the hydrogen ion concentration will be  $10^{-7}$  *M*, approximately. When this is not the case, but where the restrictions put upon eqns. (10) and (11) apply, the hydrogen ion concentration is independent of the concentration of the salt.

Finally, it should be noted that this treatment has dealt with uni-univalent salts of weak acids and weak bases. A derivation with similar strategy, but more complicated looking results, is obtained for other classes of salts of weak acids and weak bases, such as ammonium oxalate, a uni-bivalent salt.

For further information, see D. D. DEFORD, J. CHEM. EDUC., 27, 554 (1950) and J. F. BUTLER, "Ionic Equilibria, A Mathematical Approach," Addison-Wesley, Reading, Mass., 1964. An interesting related discussion can be found in C. H. LANGFORD AND R. A. BEEBE, "The Development of Chemical Principles," Addison-Wesley, Reading, Mass., 1969, pp. 179-197.