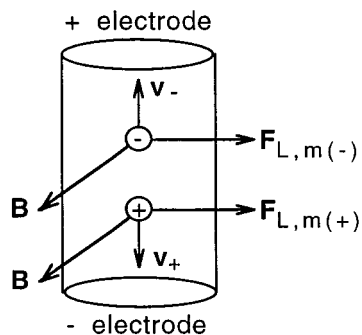Chart 2. Parallel Magnetic Lorentz Forces on Cations, $F_{L,m(+)}$, and Anions, $F_{L,m(-)}$, Migrating toward the Negative and the Positive Electrodes, Respectively

+ electrode

v_-

$\ominus$ $\longrightarrow F_{L,m(-)}$

B

$\oplus$ $\longrightarrow F_{L,m(+)}$

B

v_+

- electrode

two situations should be equal to 0.501. Experimentally it was measured ~1.1 T 0.5 in. above the center of a single magnet and ~2.2 T halfway between the two magnets.

At this point, it is obvious that, by conducting electrochemistry in the vicinity of permanent magnets, the presence of magnetic field gradients is rather unavoidable. Therefore, for a better understanding of the observed phenomena, it was decided to consider quantitatively the modes of mass transfer in space characterized by both a magnetic field and a magnetic field gradient.

2. General Theory of Mass Transfer in Dilute Electrolytic Conductors Containing Paramagnetic Species. The ensuing discussion concerns dilute solutions and redox processes induced with milli- and microelectrodes, whereas the magnetic field generated according to Ampere's law by the current flowing through the electrolytic conductor is much weaker ($<10^{-4}$ T) than the externally applied magnetic field ($1-2$ T), and its effects are not considered further.[2b,f,3a]

Always there are two kinds of magnetic forces: those applied on moving charges and those applied on magnetic dipoles.

The electromagnetic force on moving charges (the Lorentz force, F_L) is given by eq 4, where

$$F_L = q[E + v \times B] \qquad (4)$$

q and v are the charge and the velocity of the moving particle, E is the intensity of the electric field, and B is the magnetic induction.[4a] During electrolysis cations and anions move in opposite directions, so that the signs of $q_+ v_+$ and $q_- v_-$ are both positive by convention (subscripted "+" and "−" denote cations and anions, respectively). As a result, both cations and anions experience magnetic forces ($F_{L,m(+)}$ and $F_{L,m(-)}$) in the same direction (Chart 2). That creates an asymmetry in the electrolytic continuum, and since the mean free path of accelerated ions is short (on the order of the ionic diameter), both cations and anions transfer net momentum to the surrounding solvent, which from then on behaves as if the magnetic force was exerted on the entire volume element of the electrolyte containing the accelerated ions.[5a,6]

The magnetic force, F_B, acting upon the unit volume element of the electrolyte is the sum of the Lorentz forces acting upon all moving ions contained in that volume, and is given by eq 5, where

$$F_B = (n_+ q_+ v_+ + n_- q_- v_-) \times B \qquad (5)$$

n_+ and n_- are the numbers of cations and anions, respectively. The quantity $(n_+ q_+ v_+ + n_- q_- v_-)$ is the current density, i, which by definition is parallel to the velocity of the cations, v_+. Therefore, macroscopically, F_B is given by eq 6, which is of the same form

$$F_B = i \times B \qquad (6)$$

as for electronic conductors. It should be noted again that eq 6 is only an approximation, albeit a good one, because it does not account for the following: (a) the effect of the magnetic field produced by i (Ampere's law) on i itself and (b) the effect of the current that results from the dynamo created by the sweeping motion of the unit volume element in the magnetic field (refer to the Hall effect).[6a]

As it turns out, magnetic forces acting upon magnetic dipoles (which may or may not be electrically neutral) are also asymmetric and therefore result in body forces acting upon the electrolytic solution. The following analysis concerns only permanent magnetic dipoles, i.e., paramagnetic species.

Magnetic fields cause general alignment of otherwise randomly oriented distributions of atomic, molecular, or ionic magnetic dipoles, j.[4d] Because of their electrochemical interest, here we consider only dipoles with spin $^1/_2$: all free radicals generated by one-electron oxidation or reduction of diamagnetic species fall in this category. Some of those dipoles are oriented parallel and some antiparallel to the magnetic field, thus defining two energy states populated according to the Boltzmann distribution. At thermal equilibrium, the lowest state (i.e., the one with the dipole magnetic moments, m_j, parallel to the field) has an excess population, and therefore, the entire distribution has a net magnetization due to species j parallel to the field. The average magnetic moment per dipole, $\langle m \rangle_j$, in the distribution is given by eq 7,[4d] where k is the

$$\langle m \rangle_j = m^*[\tanh(m^*|B|/kT)]B/|B| \qquad (7)$$

Boltzmann constant, T is the absolute temperature, and $m^* = g(^1/_2)\mu_B$. In turn, μ_B ($= 9.274 \times 10^{-24}$ J T^{-1}) is the Bohr magneton, and g is the Lande's g factor, a dimensionless constant ~1. B denotes the effective magnetic field in the electrolytic medium, and since the permeability of a diamagnetic medium such as the electrolyte is equal to 1.00, B is considered equal to the quantity described by eq 1.[9] For diamagnetic species, both m^* and $\langle m \rangle_j$ vanish.

Saturation magnetization, namely, a near independence of magnetization on $|B|$, is encountered for $|B|/T > 1.0$.[4d,13] Typical magnetization conditions encountered in electrochemistry ($|B| \sim 1-2$ T and $T \sim 298$ K) are far from saturation and produce

(13) Craik, D. *Magnetism, Principles and Applications*; John Wiley and Sons: New York, 1997; p 29.