

is reversible. The evolutions of the two profiles,  $C_O(r, \phi, z, t)$  and  $C_R(r, \phi, z, t)$  are described by the continuity eqs 18 and 19.

$$\partial C_O(r, \phi, z, t) / \partial t = -\nabla \cdot \mathbf{J}_O \quad (18)$$

$$\partial C_R(r, \phi, z, t) / \partial t = -\nabla \cdot \mathbf{J}_R \quad (19)$$

While the flux of diamagnetic O is given everywhere by eq 16, the flux expression for paramagnetic R in the magnetic field is derived as follows.

The flux of any species  $j$  is given by eq 20,<sup>18b</sup> where  $\bar{\mu}_j$  is the

$$\mathbf{J}_j = -(C_j D_j / N_A k T) \nabla \bar{\mu}_j + C_j \mathbf{v} \quad (20)$$

magnetoelectrochemical potential of  $j$ , which, in analogy to the familiar electrochemical potential, contains the magnetic contribution in the ability of  $j$  to produce work. To express  $\bar{\mu}_j$  in terms of knowable quantities, we need to consider the contribution of the magnetostatic energy,  $U_M$ , to the total internal energy of the electrolytic solution,  $U_T$ .<sup>19</sup>

The infinitesimal change in the total internal energy of a phase,  $d\bar{U}_T$ , due to an infinitesimal change in the content of the phase in component  $j$  has the following: (a) the usual  $P$ – $V$ – $T$ – $n$  contributions of an electrically neutral, nonmagnetic phase,  $dU$ ; (b) contributions due to changes in the charge of the phase,  $dU_Q$ ; and (c) contributions due to changes in the magnetization of the phase,  $dU_M$ . In other words,

$$d\bar{U}_T = dU + dU_Q + dU_M \quad (21)$$

Now,  $dU$  is given by eq 22,

$$dU = T dS - P dV + \sum_{j=1}^{j_{\max}} \mu_j dn_j \quad (22)$$

where  $dS$  is the entropy change,  $\mu_j$  is the chemical potential of species  $j$  ( $j_{\max}$  is the total number of species in the phase), and  $dn_j$  is the change in the amount of  $j$  in moles.

On the other hand,  $dU_Q = \phi dQ$ , where  $\phi$  is the phase potential and  $dQ$  the change in the total charge of the phase.  $Q$  is given by eq 23, where  $z_j$  is the ionic charge of every species  $j$ .

$$Q = F \sum_{j=1}^{j_{\max}} z_j n_j \quad (23)$$

Therefore,  $dU_Q$  is given by eq 24.

$$dU_Q = F\phi \sum_{j=1}^{j_{\max}} z_j dn_j \quad (24)$$

Similarly, taking into consideration eqs 7 and 9,  $dU_M$  for the entire phase is given by eq 25:

(19) Haase, R. *Thermodynamics of Irreversible Processes*; Dover Publications: New York, 1990; p 64.

$$dU_M = -N_A \sum_{j=1}^{j_{\max}} (m^* / |\mathbf{B}|) [\tanh(m^* |\mathbf{B}| / kT)] \mathbf{B} \cdot \mathbf{B} dn_j \quad (25)$$

Overall, taking into consideration eqs 22, 24, and 25, eq 21 is transformed into eq 26.

$$d\bar{U}_T = T dS - P dV + \sum_{j=1}^{j_{\max}} [\mu_j + F\phi z_j - N_A (m^* / |\mathbf{B}|) [\tanh(m^* |\mathbf{B}| / kT)] \mathbf{B} \cdot \mathbf{B}] dn_j \quad (26)$$

Equation 26 is of the form,

$$d\bar{U}_T = T dS - P dV + \sum_{j=1}^{j_{\max}} \bar{\mu}_j dn_j \quad (27)$$

where the magnetoelectrochemical potential,  $\bar{\mu}_j$ , of a species  $j$  with spin  $1/2$  in a given phase is defined now via eqs 26 and 27 by

$$\bar{\mu}_j = \mu_j + F\phi z_j - N_A (m^* / |\mathbf{B}|) [\tanh(m^* |\mathbf{B}| / kT)] \mathbf{B} \cdot \mathbf{B} \quad (28)$$

Equation 28 is quite general, but again for magnetization conditions far from saturation  $\tanh(m^* |\mathbf{B}| / kT) \approx m^* |\mathbf{B}| / kT$ , and eq 28 becomes

$$\bar{\mu}_j = \mu_j + F\phi z_j - N_A [(m^*)^2 / kT] \mathbf{B} \cdot \mathbf{B} \quad (29)$$

Finally, since  $\mu_j = \mu_j^p + N_A kT \ln C_j$  (where  $\mu_j^p$  is the standard chemical potential of  $j$  in the phase),<sup>18b</sup> by introducing eq 29 into eq 20 we obtain eq 30 as the expression for the flux of a paramagnetic species  $j$  in a magnetic field gradient typical of electrochemical experimental conditions.

$$\mathbf{J}_j = -D_j \nabla C_j - (z_j C_j D_j F / N_A k T) \nabla \phi + 2 C_j D_j (m^* / kT)^2 \mathbf{B} \cdot \nabla \mathbf{B} + C_j \mathbf{v} \quad (30)$$

Equation 30 indicates that even in the absence of convection (as for example in the stagnant layer close to an electrode) the field gradient causes a drift of paramagnetic species toward areas of higher field. In this regard, eq 30 is very relevant to recent reports on magnetic focusing at magnetic electrodes<sup>2g,h</sup> and on magnetophoresis of tagged polymers,<sup>20</sup> or paramagnetic ions.<sup>21</sup> This magnetophoretic mode of transport resembles concentration gradient-driven diffusion or electric field gradient-driven migration.<sup>22</sup>

### 3. Voltammetry in the Magnetic Field of Permanent Magnets. Figure 2 shows voltammograms as a function of the

(20) Barkema, G. T.; Schutz, G. M. *Europhys. Lett.* **1996**, *35*, 139.

(21) Fujiwara, M.; Kodoi, D.; Duan, W.; Tanimoto, Y. *J. Phys. Chem. B* **2001**, *105*, 3343.

(22) It is noted that magnetophoretic drift of ion radicals (i.e., of charged paramagnetic species) would create a charge separation, which is expected to establish an electric potential opposing further magnetic field-induced drift. That potential difference,  $\Delta\phi$ , between two points at different  $|\mathbf{B}|$ 's, can be calculated from the magnetoelectrochemical potential (eq 29) and is given by  $\Delta\phi = [N_A (m^*)^2 / z_j F k T] \Delta(|\mathbf{B}|^2)$ .