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Comments on "Redox Potentials by Equilibration," by W. G. Breck[1]

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Breck (1972) has proposed a new approach for determining the "redox level" (Eh) in aerated natural waters and has described an electrode arrangement which, supposedly, is capable of accurately measuring Eh in such waters. The apparatus described by Breck is composed of a solution of a known oxidation-reduction couple (O^*/R^*) connected to a test solution (O/R) by a graphite and saturated KCl bridge. It is claimed that, at equilibrium, the auxillary solution O^*/R^* will assume the Eh of O/R. Hence, the Eh of the test solution (O/R) can be determined by measuring the redox potential of O^*/R^* by means of a platinum electrode relative to a reference electrode.

The schematic diagram in Fig. 1 represents the arrangement proposed by Breck as it depicts all the electrochemical half cells involved. Breck's basic assumption is that, at equilibrium (i.e., when the loop current drops to zero), the "redox level" of O^*/R^* is equal to that of O/R, and hence, E (Fig. 1) represents the Eh of O/R. However, Fig. 1 reveals that this assumption can be correct only if the graphite electrode is capable of measuring the "redox level" in both O/R and O^*/R^*.

This can be shown in the following way: Assume that the electrode arrangement proposed by Breck is indeed functioning as claimed. At equilibrium, the oxidation-reduction potentials of O/R and O^*/R^* are identical (as hypothetically assumed), hence:

$$E' = E_{O/R} + Ej_{O/R} = E_{O^*/R^*} + Ej_{O^*/R^*}, \qquad (1)$$

or (neglecting the junction potentials):

$$E' = E_{O/R} = E_{O^*/R^*}. \qquad (2)$$

Hence, the graphite electrode should be capable of directly measuring the redox potentials in O/R and O*/R. If, however, the graphite electrode is not reversible to oxidation-reduction reactions in O/R and/or O*/R*, the auxillary solution O*/R* will not reach the same "redox level" as that of O/R.

Breck's implicit *a priore* assumption—that the graphite electrode can measure redox potentials in aqueous solutions—is not supported by experimental or theoretical evidence. Furthermore, there is evidence that this assumption is probably incorrect. Berl (1943), Weisz and Jaffe (1948), and Yeager et al.
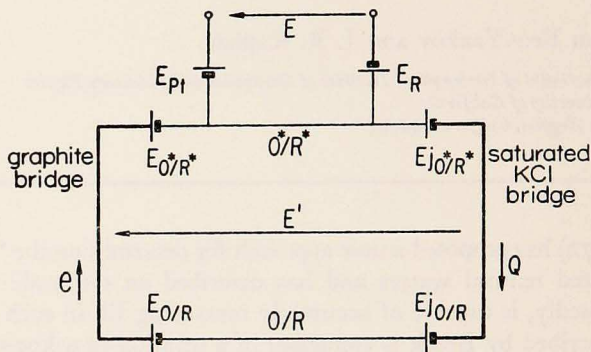

Figure 1. Schematic representation of the cell arrangement proposed by Breck (1972). The half cells $E_{O/R}$ and $E_{O*/R*}$ represent the graphite half cells $Ej_{O/R}$ and $Ej_{O*/R*}$, the liquid junction potentials; E_{pt} the platinum electrode half cell; and E_R the liquid junction potential of the reference electrode relative to which the platinum electrode is measured.

(1964) found that the graphite electrode is reversible to the redox couple oxygen/peroxide (which, according to Breck, controls the "redox-level" in aerated natural waters) *only* at alkaline solutions in the range 0.1 to 5 M KOH. These alkaline conditions are clearly outside the range of natural waters (Baas-Becking, et al. 1960), hence the use of the graphite electrode for redox potential measurement in these waters is eliminated. In addition, proper operation of the Breck cell requires that the graphite electrode be thermodynamically reversible in a solution of an oxidation-reduction couple such as ferric-ferrous. No evidence of this effect is given, thus casting doubt on its applicability as a redox electrode.

Incidentally, if the graphite electrode can indeed measure redox potentials in O/R (which it probably cannot), why bother with a complicated cell arrangement as described by Breck. It seems that the author has used illogical reasoning. In order to *electrochemically* equilibrate O*/R* with O/R (as proposed), one must assume reversibility of electrode reactions to both O*/R* and O/R. If the graphite electrode is indeed reversible to oxidation-reduction reactions, why not measure directly the potential $E_{O/R}$ relative to a conventional reference electrode?

There are other difficulties with the cell arrangement proposed by Breck. For example, use of the KCl bridge as an electronic conductor may result in unpredictable large liquid junction potentials [eq. (1)]. An electrolytic solution is not an electronic conductor, but rather an ionic conductor. Hence, the mechanism of charge transfer through the KCl bridge is a complicated process that may not only cause abnormally large junction potentials but may also modify the composition of O*/R*. However, unlike the basic problem regarding the applicability of the graphite electrode, these second-order difficulties can probably be overcome.

In the second part of his paper, Breck discussed the problem of redox control in aerated natural waters and presented arguments that support the view that the oxygen/peroxide couple controls the oxidation-reduction poise in these waters. Without going into the question of whether this view is acceptable (we believe that the arguments can be accepted only if supported by sound experimental evidence), we would like to comment on the concept of redox level of aerated natural waters. It is generally accepted (Stumm and Morgan 1970: 300–377, Broecker and Oversby 1971: 277–278, Berner 1971: 118–119) that aerated natural waters are not in thermodynamic equilibrium with respect to *all* their oxidation-reduction couples. Therefore, there is no single redox level that would describe all the couples. Furthermore, it is highly probable that certain oxidation-reduction couples are more important than others in a given geochemical process. Some couples may be important in short-term processes whereas others may be important in long-term processes extending over geological time. It would appear, then, that the concept of "redox level of aerated natural waters" is hopelessly ambiguous and may not be rigorously defined.

The platinum electrode has long been used as a rough indicator of oxidation-reduction levels in natural waters. Despite its many shortcomings, it has been a useful empirical indicator in numerous geochemical and hydrological studies. It is yet to be shown that the electrode proposed by Breck can match the questionable performance of the platinum electrode. Judging from Breck's data (1972: table 1), the cell does not seem to respond to a variety of conditions that may be met in natural-water measurements. The Eh range of nine surface saline-water measurements was $0.51 \pm .02$ V and the range of six nonsaline waters (including one hot spring) was $0.50 \pm .01$ V. However, a sulfide-smelling spring (Warner Hot Springs) yielded a value of 0.42 V, showing a potential shift of only 0.08 V between oxidizing and reducing waters. By comparison, the platinum electrode displayed a potential shift of 0.30 V. Although no pH data were provided, it would not be surprising if the total spread in pH between fresh water and seawater was larger than 1.0 pH unit. Assuming Breck's suggestion that the reactions described with eqs. (6) and (7) and Fig. 7 are the mechanisms for redox control of aerated water, it is obvious that H^+ enters into the equation. The resultant Eh shift expected over a 1-pH unit range should

be ± 0.06 V. The apparent lack of response to sulfide on the one hand and to pH on the other points to either a lack of reversibility of the graphite electrode or to polarization poisoning.

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