# Master Variables and Activity Scales

LARS GUNNAR SILLÉN

Royal Institute of Technology (KTH), Stockholm, Sweden

*The infinite dilution activity scale is useful for ionic equilibria in fresh waters, but for equilibria in sea water one gains precision by applying an ionic medium activity scale. Measuring pH in sea water gives less information than total alkalinity and total carbonate. Calculations on redox equilibria are simplified by introducing the master variable* $pE = -\log\{e^-\}$.

The equilibrium law (law of mass action) in its logarithmic form gives simple linear relationships between the activities of the reactants (*e.g.*, Equation 1). In the following text, the curled brackets represent activities, and the square brackets concentrations.

$$\log K_a = \log\{H^+\} + \log\{A^-\} - \log\{HA\} \qquad (1)$$

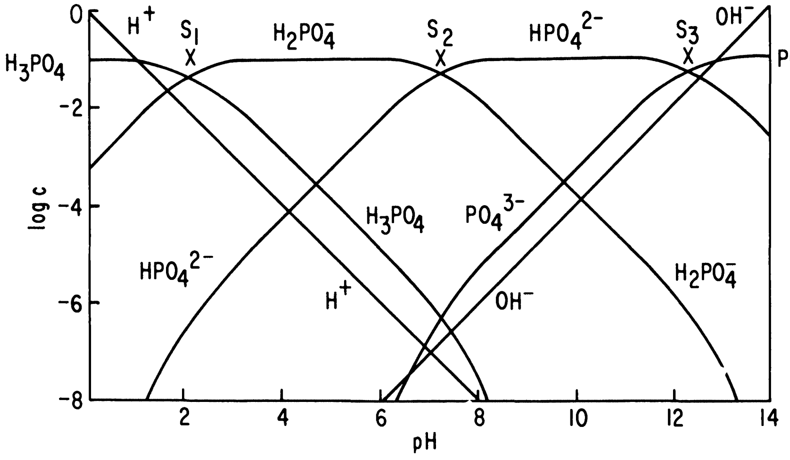
One can add or subtract log $K$ values in the same way that one adds or subtracts the corresponding reaction formulas. An example is given below for 25°C., infinite dilution (*18*).

$$(+)\ CaCO_3(s) + CO_2(p\text{ atm.}) + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^- \qquad \log K = -5.83$$
$$(-)\ CO_2(p\text{ atm}) + H_2O \rightleftharpoons H_2CO_3 \qquad \log K = -1.46$$
$$(+)\ H^+ + HCO_3^- \rightleftharpoons H_2CO_3 \qquad \log K = 6.35$$
$$(-)\ H^+ + CO_3^{2-} \rightleftharpoons HCO_3^- \qquad \log K = 10.33$$

Summing up, one obtains:

$$CaCO_3(s) \rightleftharpoons Ca^{2+} + CO_3^{2-}$$
$$\log K = -5.83 + 1.46 + 6.35 - 10.33 = -8.35 \qquad (2)$$

The logarithmic form lends itself to graphical presentation. For example, in a system containing a number of acid-base systems of known total concentrations, the concentration of each individual species is a unique function of the master variable log $[H^+]$, which may be represented in a logarithmic diagram. In Figure 1, for a system with total phosphate concentration 0.1*M*, the log (concentration) of the various species is given as a function of pH. The linear portions of the curves point toward the system points with coordinates (log total concentration, log acidity constant). Such diagrams and their uses are more fully discussed in Ref. *13*.



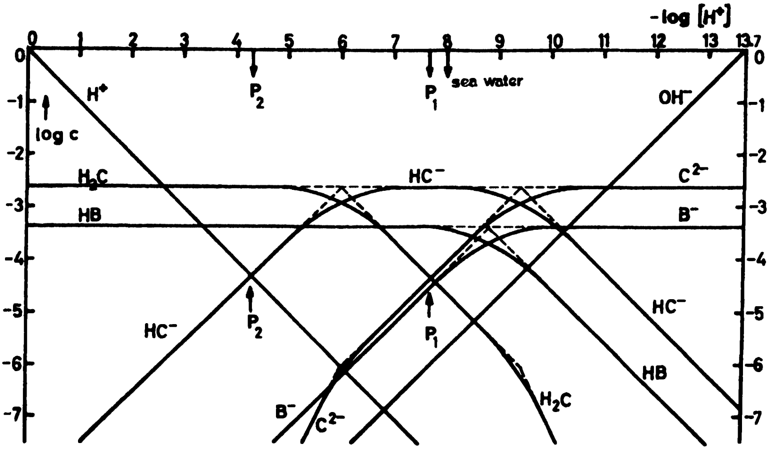
L. G. Sillén, "Treatise on Analytical Chemistry," Interscience

*Figure 1. Logarithmic diagram of log* c *as a function of pH for solutions with total phosphate concentration 0.1*M*, assuming* $pK_1 = 2.1$, $pK_2 = 7.2$, $pK_3 = 12.3$, *and* $pK_w = 14.0$ (13)

Another example is Figure 2, which is a diagram for a sample of sea water (*7*). It shows the log (concentration) for the species in the carbonate system ($H_2C$, $HC^-$, $C^{2-}$) and the borate system ($HB$, $B^-$) at various pH. At the log $[H^+]$ of the sea water sample, one may read the concentrations of the two predominating species ($HCO_3^-$ and $H_3BO_3$) and of the minor species. One can also determine the change in concentrations as the $[H^+]$ is altered—*e.g.*, by adding acid. It is immediately obvious that there will be two equivalence points (points of minimum buffer capacity), namely, $P_1$ and $P_2$.

For other types of equilibria other master variables can be used—*e.g.*, log $[Cl^-]$ or log $[Br^-]$ for halogeno complexes, p*E* (*see below*) for redox equilibria, and log $p(O_2)$ for equilibria between oxides and gas phases (*12*).

Such diagrams of course contain the same information as used in numerical calculations—*i.e.*, equilibrium conditions for the various reactions, and the mass balance conditions. Their advantage is in giving in a single glance a clear picture of the situation.



Tellus

*Figure 2. Logarithmic pH diagram for sea water, assuming log* $[B]_{tot} = -3.37$, *log* $C_t = -2.62$, *and the following* ($-\log K_a$) *values: 6.0 for* $H_2CO_3$, *9.4 for* $HCO_3^-$ *and 8.8 for* $B(OH)_3$, *and log* $K_w = -13.7$ *(only the order of magnitude is representative). Arrows give log* $[H^+]$ *for sea water and for two equivalence points (points of minimum buffer capacity),* $P_1$ *(corresponding to* $HB + HC^-$*) and* $P_2$ *(corresponding to* $HB + H_2C$*) (7)*

## The Ionic Medium Method

In Figure 2 one may ask whether concentrations or activities are meant, especially for $H^+$. Actually, both are since one should use a scale where they are identical.

In the last few decades an increasing number of workers interested in complicated ionic equilibria have been using the "ionic medium" method (*3*). Instead of water, as a solvent one uses a salt solution of fairly high concentration, such as 2*M* NaCl or 3*M* $LiClO_4$, keeping the concentrations of the reacting species much lower than that of the medium ions.

Since some reactants are usually ionic, one must decide on some mixing rule. Usually the concentration of an individual medium ion or the ionic strength is kept constant. (The mixing rule is indicated by 3*M* $Na(ClO_4)$, 3*M* $(Na)ClO_4$ in the "Tables of Stability Constants" (*18*).) Whichever rule one uses, this will not change the definitions below.

The concentrations are then used instead of the activities in various thermodynamic expressions (*e.g.*, the equilibrium law, and Nernst's equation for the e.m.f.). Some physical chemists are suspicious of this method. However, it is just as thermodynamic as the traditional one, the only difference being that another activity scale is used.

### *Activity Scales*

Activity $\{A\}$ is defined by the chemical potential $\mu_A$ as shown in Equation 3.

$$\mu_A = \mu_A^* + RT \ln\{A\} = \mu_A^* + RT \ln \gamma_A[A] \qquad (3)$$

Here, $\mu_A^*$ is a constant, which defines the activity scale, and $\gamma_A$ is the activity coefficient. For the moment we will disregard the units of concentration (mole fraction, moles per kg. solution, moles per kg. water). Changing to a new activity scale means that $\mu_A^*$ is shifted by a constant and that all activities are multiplied by the same factor.

In treating ionic equilibria in aqueous solution, two activity scales have proved especially useful. The first is the traditional infinite dilution activity scale, which is defined in such a way that the activity coefficient $\gamma_A = \{A\}/[A]$ approaches unity as the solution approaches pure water. One might refer to this scale as the fresh water scale.

The "ionic medium" activity scale, on the other hand, is so defined that the activity coefficient, $\gamma_A = \{A\}/[A]$ approaches unity as the solution approaches the pure solvent (in this case the ionic medium)—*i.e.*, when the concentrations go toward zero for all other species than water and the medium ions.

Experience shows that the activity coefficients on this scale stay near unity (usually within experimental error) as long as the concentrations of the reactants are kept low, say less than 10% of the concentrations of the medium ions. The activity ( $\approx$ concentration) of several ions, notably $H^+$, can be determined conveniently and accurately by means of e.m.f. methods, either with or without a liquid junction. In the latter case the liquid junction potential is small (mainly a function of $[H^+]$) and easily corrected for (3). The equilibrium constant for any reaction, on the ionic medium scale, may then be defined as the limiting value for the concentration quotient:

$$K = \lim Q \text{ (pure medium)} \qquad (4)$$

where *e.g.*,

$$Q = [H^+][A^-]/[HA] \qquad (4a)$$

In usual measurements at low reactant concentrations, the deviations of $Q$ from $K$ are usually smaller than the experimental errors; hence, it is preferable to set $K$ equal to the average of $Q$ rather than to extrapolate according to Equation 4.

Since no extrapolation is needed, equilibrium chemists working with an ionic medium scale have often not bothered to define rigidly the constant with which they are working. Sometimes they have used a misleading nomenclature—*i.e.*, for a thermodynamic equilibrium constant $K$

valid in an ionic medium, they have used the term "concentration quotient" or "apparent constant" as distinguished from the so-called "true thermodynamic equilibrium constants" on the infinite dilution activity scale. As a matter of fact, equilibrium constants on an ionic medium scale are thermodynamically as well defined as those on the infinite dilution scale, and often they can be measured much more accurately if one wishes to do so (*11*).

Since the oceans of the world contain an ionic medium of practically constant composition, ocean chemists should use the ionic medium approach when studying the equilibria of minor components, such as the carbonate species and the borate species. A model sea water might contain, in 1 kg. solution, 0.478 mole $Na^+$, 0.064 mole $Mg^{2+}$, 0.550 mole $Cl^-$ and 0.028 mole $SO_4^{2-}$.

### *Equilibria With the Medium*

Equilibrium studies in dilute aqueous solutions cannot alone help to distinguish between species that differ only by varying amounts of water. One may learn, for example, that a boron species exists with one boron atom and no charge, and another with one boron atom and the charge −1. One may write them (because of other evidence) as $B(OH)_3$ and $B(OH)_4^-$, but as far as the equilibrium data are concerned what we call $[B(OH)_4^-]$ might well be a sum of the concentration of $BO_2^-$, $H_2BO_3^-$, and $B(OH)_4^-$. This must also be understood when we use conventional formulas for the concentrations of, say $H^+$ and $H_2CO_3$:

$$\text{“}[H^+]\text{”} = \Sigma[H_{2n+1}O_n^+];\quad \text{“}[H_2CO_3]\text{”} = \Sigma[CO_2(H_2O)_n] \qquad (5)$$

We cannot distinguish between such species simply because we do not vary the water activity $\{H_2O\}$. Working with an ionic medium, we also keep the activities of the medium ions practically constant, and so we cannot distinguish between species containing various amounts of the medium ions. Hence, one must understand that the formulas for various species include an unknown number of water molecules and medium ions. For instance, if our ionic medium is the model sea water referred to above, we would mark true concentrations by asterisks.

$$\begin{aligned}
&[H^+] = [H^+]^* + [HSO_4^-]^* + \ldots \\
&[Mg^{2+}] = [Mg^{2+}]^* + [MgSO_4]^* \ldots \\
&[CO_3^{2-}] = [CO_3^{2-}]^* + [MgCO_3]^* + [NaCO_3^-]^* + \ldots \\
&[HCO_3^-] = [HCO_3^-]^* + [MgHCO_3^+]^* + \ldots \qquad (6)
\end{aligned}$$

Note that we can distinguish between $HCO_3^-$ and $CO_3^{2-}$ since both carbonate and $H^-$ are minor species and do not belong to the medium ions. The uncertainty expressed in Equation 6 might be thought of as a limitation of the ionic medium method, but it is also an advantage since one need not bother about the equilibria of complex formation with $Mg^{2+}$ and $Na^+$ which are surely hard to measure accurately, and which are now eliminated by definition. The remaining equilibria (between metal ions, $H^+$, $CO_3^{2-}$, borate etc.) could, on the other hand, be determined quite accurately. Hence, in ocean chemistry one would use an ionic medium activity scale rather than the infinite dilution scale. On the other hand, for equilibria in fresh waters, the ionic concentrations are so low that one may, with some confidence, use the common approximation formulas to estimate the ionic activity coefficients on the infinite dilution scale. The fresh water scale would seem logical for such waters.

## *What is pH?*

The quantity pH has been defined at least three different ways (*2*). Sørensen's (*16*) original definition was $pH = -\log[H^+]$. Those using an ionic medium scale may use this definition since one can usually measure $-\log[H^+] = -\log\{H^+\}$ rather accurately.

The activity definition (*17*) on the "infinite dilution" scale, $paH = -\log\{H^+\} = -\log \gamma_H - \log[H^+]$ was experimentally studied by Bjerrum and Unmack (*4*). This definition is not rigid because of the intrinsic uncertainty in defining individual ionic activities. Depending on the precision required, it is usually stated that the approximations used to estimate $\gamma_H$ breakdown at some ionic strength between 0.01 and 0.2*M*.

An operational definition has been repeatedly suggested (*5*, *9*) and that sponsored by IUPAC is based chiefly on the work of Bates (*1*, *2*). The pH is defined in terms of a cell—*e.g.*, calomel electrode||solution|glass or hydrogen electrode.

As cell solution for this example one uses, in two different experiments, the unknown solution (x) and a standard buffer solution (s), whose pH($pH_s$) has been estimated so as to approach the second definition. Comparing the e.m.f.'s gives

$$pH_x - pH_s = -(E_x - E_s)(RTF^{-1}\ln 10)^{-1} \qquad (7)$$

With this definition a reproducible number will always result. On the other hand the $pH_x$ so obtained does not correspond exactly to the second definition since it contains the uncertainty in the definition of $\gamma_H$ and in addition an unknown difference in the liquid junction potential which may be important, especially if the solution is not very dilute. If similar solutions are compared, however, differences in pH may give accurate ratios between $H^+$ activities or concentrations.

Many measurements of pH in sea water have been recorded, usually to within two decimals. If one used an operational definition and could teach oceangoing chemists to apply the same standards of accuracy, one should obtain pH values measured by e.m.f. that would be comparable within ±0.01 if taken at the same temperature and salinity. Even this aim does not seem to be fulfilled at present. Moreover pH will vary if a water mass is brought to a different pressure and temperature, even if there is no change in chemical composition, and it is hard to make a meaningful, accurate comparison of pH values at different pressure and temperature. It would seem better to measure quantities

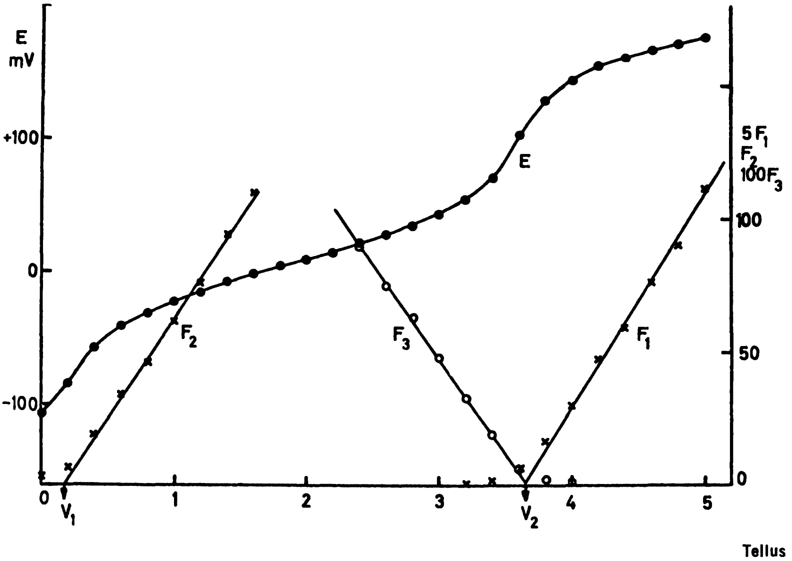


*Figure 3. E.m.f. titration curve for 154 grams sea water with* v *ml. (0.1000*M *HCl + 0.4483*M *NaCl).* E *(mv.) for the cell: reference electrode|solution|glass electrode* vs. v *(ml).* $F_1$, $F_2$, *and* $F_3$ *are Gran functions for finding the equivalence points* $v_1$, $v_2$ *(corresponding to* $P_1$ *and* $P_2$ *in Figure 2) (7)*

that are conservative and independent of $p$ and $T$, such as the total carbonate concentration $C_t$, the total alkalinity, $A_t$, and the difference ($A_t - C_t$). Both $C_t$ and ($A_t - C_t$) can be obtained from a single e.m.f. titration of a sea water sample with acid which gives the two equivalence points in the titration curve, $P_1$ and $P_2$ indicated in Figure 2. The amount of acid added at $P_1$ corresponds to ($A_t - C_t$) and that added between $P_1$ and $P_2$ to $C_t$. Figure 3 gives $E$ *vs.* ml. acid from a preliminary experiment by Dyrssen and co-workers (7). The lines are plots of Gran functions to find the equivalence points. The method is inherently quite accurate, and it seems more meaningful to collect values for $C_t$ and ($A_t - C_t$) for various sea water masses than to assemble large tables of pH values.

### *Redox Equilibria*

In oxidation-reduction equilibria, the common reagent is the electron $e^-$, and matters are simplified considerably if one treats the electron like any other reagent, $H^+$, $Ag^+$, $Cl^-$, etc. (Note that neither of these exists free and unhydrated in aqueous solutions). Clark has suggested (*6*) using $\{e^-\}$, and Jørgensen (*8*) has suggested the definition:

$$pE = -\log\{e^-\} \qquad (8)$$

This is analogous to the second definition of pH. The electron activity scale is fixed to the hydrogen scale by $H^+ + e^- \rightleftarrows \frac{1}{2}H_2(g)$; $\log K = 0$. Hence, $pE = 0$ at a standard hydrogen electrode, and for any system at equilibrium we find the relationship between our new quantities and the reversible redox potential, $e$ (or $E_h$)

$$e\ (=E_h) = -RTF^{-1}\ln\{e^-\} = (RTF^{-1}\ln 10)pE \qquad (9)$$

$$pE = e/(RTF^{-1}\ln 10) \qquad (9a)$$

The value of $(RTF^{-1}\ln 10)$ is 59.155 mv. at 25°C. Once the $\{e^-\}$ scale has been defined, we may begin to use equilibrium constants on that scale. For instance, inserting $\log p(O_2) = -0.68$, $\log\{H^+\} = -8.1$ and $\log\{H_2O\} = -0.01$ into the equilibrium constant for

$$\tfrac{1}{2}O_2(g) + 2H^+ + 2e^- \rightleftarrows H_2O(l); \qquad \log K = 41.55$$

we find that $pE = 12.5$ in sea water at equilibrium with air at 25°C.

Values for $\log K$ for various redox reactions are given in Ref. *18* together with the traditional standard potential values. Those who prefer to express the electron activity in volts rather than on a scale similar to that for other reagents should remember that at one time some physical chemists opposed expressing acidity by $[H^+]$ or pH. They claimed quite correctly that what one measures is really not a concentration but an e.m.f., and thus they found it more logical to measure the acidity, not by $[H^+]$ or its logarithm, but rather by the "acidity potential," a quantity in volts.

Log $K$ values for redox reactions may be added just like any other log $K$ values—*e.g.*, Reaction 10 (*18*).

$$(+)\ Ag_2S(s) + 2H^+ + 2e^- \rightleftarrows 2Ag(s) + H_2S(g) \qquad \log K = -1.22$$

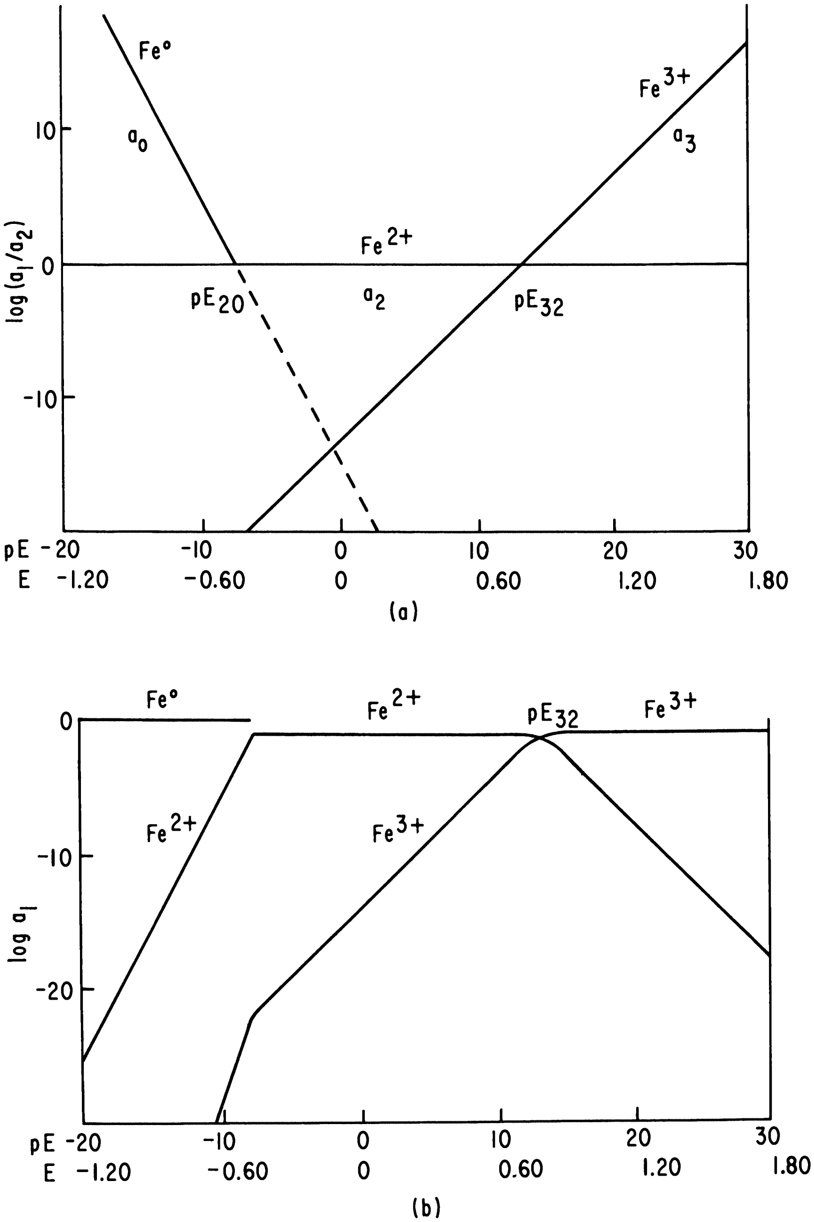
$$(-2)\ Ag^+ + e^- \rightleftarrows Ag(s) \qquad \log K = 13.514$$

Summing up:

$$Ag_2S(s) + 2H^+ \rightleftarrows 2Ag^+ + H_2S(g)$$

$$\log K = -1.22 - 2 \times 13.514 = -28.25 \qquad (10)$$

Reaction 11 is taken from calculations (*14*) of possible concentrations of



L. G. Sillen, "Treatise on Analytical Chemistry," Interscience

*Figure 4. Redox diagrams for Fe. (a) Log* (a/$\{Fe^{2+}\}$) *as a function of pE for* $Fe^0$, $Fe^{2+}$ *and* $Fe^{3+}$. *Where the* $Fe^0$ *line is broken, solid Fe cannot exist at equilibrium. (b) Log* a *as a function of pE for* $Fe^0$, $Fe^{2+}$, *and* $Fe^{3+}$. *The total Fe concentration is assumed to be 0.1*M *except in the range where solid Fe exists at equilibrium* (13)

various Fe species in sea water at equilibrium with FeOOH(s). We may combine log *K* values as follows:

$$\mathrm{FeOOH(s)} + 3\mathrm{H}^{+} \rightleftarrows \mathrm{Fe}^{3+} + 2\mathrm{H_2O} \qquad \log K = 4.0$$

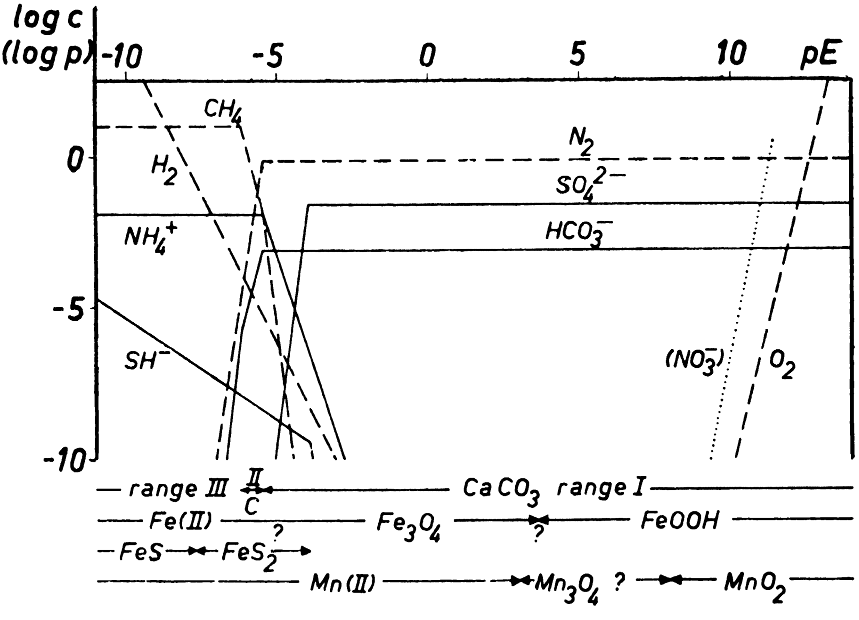
$$\mathrm{Fe}^{3+} + e^{-} \rightleftarrows \mathrm{Fe}^{2+} \qquad \log K = 13.0$$

Summing up:

$$\mathrm{FeOOH(s)} + 3\mathrm{H}^{+} + e^{-} \rightleftarrows \mathrm{Fe}^{2+} + 2\mathrm{H_2O} \quad \log K = 17.0 \qquad (11)$$

Introducing the values of pH = 8.1 and pE = 12.5 we find $\log\{\mathrm{Fe}^{2+}\} = 17 - 3\mathrm{pH} - \mathrm{p}E = -20$, which indicates that $\mathrm{Fe}^{2+}$ is not likely to explain the measured concentration of Fe in sea water (around $10^{-7.2}M$).

Using p*E* as the master variable, one may construct logarithmic diagrams. Figure 4 shows two diagrams (*13*) for the equilibria Fe(0, II, III), at the maximum total concentration 0.1*M*. Figure 4b corresponds to the acid-base diagram in Figure 1; for p*E* > 13, $\mathrm{Fe}^{3+}$ predominates in the solution; for p*E* < 13, $\mathrm{Fe}^{2+}$ does; at low p*E*, solid Fe(s) precipitates, and the activities of the dissolved species decrease sharply. Figure



Arkiv Kemi

*Figure 5. Redox diagram giving, as functions of pE, log* c *(solid) or log* p *(broken) for the main variable species in a "model system" corresponding to sea water + air + sediments. At the lower end the ranges are indicated in which various solids would be stable* (15)

4a shows a relative logarithmic diagram, with $\log\{Fe^0\} - \log\{Fe^{2+}\}$ and $\log\{Fe^{3+}\} - \log\{Fe^{2+}\}$ as functions of p*E*. Figure 5 (*15*) shows for a model, representing the real system air + ocean + sediments, how the concentrations or activities of the most important species would vary with p*E*. Our present state corresponds to $pE = 12.5$, and points to the left may to some extent resemble earlier states of the system when it was oxidizing less than now. We can, for instance, see how carbon is transformed from carbonate to C(s) and $CH_4$; nitrogen from $N_2$ to $NH_4^+$ and sulfur from sulfate to $FeS_2$(s). The lower part of the diagram indicates the solid phases present in various ranges.

If one has many calculations to make on redox equilibria, it is certainly practical to change over to the p*E* scale rather than to work with voltages. When I tried to survey the equilibria in the ocean (*14*), I saved time this way even if I had to calculate all the log *K* values first. Once that was done, there were no more divisions and multiplications by multiples of 0.05916, and there was less chance of making mistakes.

The literature contains many values for $E_h$ that have been obtained by placing a Pt electrode and a calomel electrode into the water sample (or mud). The oxidizing properties in the long run are usually determined by $[O_2]$, but $E_h$ measured in this way for a natural sample probably never gives the reversible value for the $O_2$ couple but depends on some minor constituents in the solution or impurities in the electrode. This point will be dealt with more fully in another chapter (*10*). If one uses p*E* values in calculations, there is less chance that the conclusions will be compared with dubious $E_h$ values.

## *Literature Cited*

(1) Bates, R. G., Guggenheim, E. A., *Pure Appl. Chem.* **1**, 163 (1959).
(2) Bates, R. G., "Determination of pH," Wiley, New York, 1964.
(3) Biedermann, G., Sillén, L. G., *Arkiv Kemi* **5**, 425 (1953).
(4) Bjerrum, N., Unmack, A., *Kgl Danske Videnskab Selskab, Mat-fys Medd.* **9**, No. 1 (1929).
(5) Clark, W. M., *Ind. Eng. Chem.* **28**, 620 (1936).
(6) Clark, W. M., *Hyg. Lab. Bull.* **151**, 1 (1928).
(7) Dyrssen, D., Sillén, L. G., *Tellus* **19**, 110 (1967).
(8) Jørgensen, H., "Redox-målinger," p. 10, Gjellerup, Copenhagen, 1945.
(9) MacInnes, D. A., *Science* **108**, 693 (1948).
(10) Morris, J. C., Stumm, W., ADVAN. CHEM. SER. **67**, 270 (1967).
(11) "Recommended Symbols for Equilibrium Constants," *IUPAC Inform. Bull.* **26**, 25 (1966).
(12) Sillén, L. G., Rengemo-Anderson, T., *Svensk Papperstidn.* **55**, 622 (1952).
(13) Sillén, L. G., "Treatise on Analytical Chemistry," I. M. Kolthoff and P. J. Elving, eds., Part IB, Chap. 8, 1959.
(14) Sillén, L. G., *Am. Assoc. Advan. Sci. Publ.* **67**, 549 (1961).
(15) Sillén, L. G., *Arkiv Kemi* **25**, 159 (1966).

(16) Sørensen, S. P. L., *Medd Carlsberg Lab* 8, 1 (1909); *Biochem. Z.* **21**, 131 (1909).

(17) Sørensen, S. P. L., Linderstrøm-Lang, K., *Medd Carlsberg Lab* **15**, No. 6, (1924).

(18) "Stability Constants," *Chem. Soc. Spec. Publ.* **17** (1964).

RECEIVED April 15, 1966.