

ON THE MERIT OF DEFINING AND APPLYING IONIC MEDIUM  
ACTIVITY SCALES — A REPLY TO A COMMENT BY DYRSSEN,  
JOHANSSON AND WEDBORG

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The main points raised by Dyrssen et al. (this issue, pp. 275–279 in their comment on our paper (Sass and Ben-Yaakov, 1977) are summarized as follows:

- (1) A comparison is made between the ionic composition of Dead Sea waters (DSW) and the ionic composition of seawater (SW).
- (2) The expected value for  $K'_2$  in DSW is estimated and compared to our experimental results and a suggestion is made that our values for  $pK'_2$  are too low ( $K'_2$  too high) because they do not agree with the estimate.
- (3) The scatter in the ratio  $A/C$  calculated from our reported results for  $A$  and  $C$  is interpreted as a lack of precision in the determination of  $C$ .
- (4) The similarity between our treatment and the Gran function is pointed out.
- (5) Experimental results of an HCl titration of synthetic DSW are presented along with the values of  $pK_1^*$  and  $pK_2^*$  derived by an iteration method favored by Dyrssen et al. Since the scatter in  $p(K_2^*/K_1^*)$  derived by Dyrssen et al. is smaller than the scatter of  $p(K'_2/K'_1)$  calculated from our results, a conclusion is drawn as to lack of accuracy in our experimental and analytical procedures.
- (6) It is suggested that direct curve fitting of the data to the titration equation is better than the computation method used by us.
- (7) The advantage of ionic medium activity and pH scales is stressed, suggesting that our experimental procedure introduces unknown liquid junction potentials and poorly defined activity scale for  $H^+$ .

The following is a point-by-point reply to the comments of Dyrssen et al.

(1) *The composition of Dead Sea waters (DSW)*

Dyrssen et al. open their note with a statement concerning the composition of DSW (DSB in their notation). In order to correct misinterpretation of the

geochemical data of DSW, we should like to point out that, unlike seawater, the ionic ratios in DSW are not constant. Whereas salinity (or chlorinity) uniquely defines the ionic composition of seawater, the ionic composition of DSW is variable. According to Neev and Emery (1967) TDS of the northern basin of the Dead Sea covers a 10% range, Mg/Cl and Ca/Cl ratios show variations of 5.2% and 5.9%, respectively, and (Mg + Ca) molarity changes between 1.9 and 2.2, i.e. by about 13%. Much larger variations are found in the southern basin of the Dead Sea which is practically cut off from the northern basin and consequently is being dried out.

(2) *Theoretical estimate of  $pK'_2$*

Dyrssen et al. estimated the expected increase in  $pK'_2$  in DSW as compared to SW. Based on this estimation they suggest that our results for  $pK'_2$  (Sass and Ben-Yaakov, 1977) are too low ( $K'_2$  too high). Also, although not explicitly stated, the results for  $K_2^*$  as defined and determined by Dyrssen et al. on synthetic DSW seem to agree well with their estimate for  $K_2^*$  in DSW. It should be pointed out, however, that the method used by Dyrssen et al. to estimate  $K'_2$  in DSW is based on an erroneous assumption and hence any correlation between this estimate and experimental results is fortuitous. The estimate is based on the following reasoning: The increase in  $K'_2$  (and  $K_2^*$  as defined by Dyrssen et al.) is mainly due to ion-pair formation. For carbonate ions, major association occurs with calcium and magnesium (Garrels and Thompson, 1962; Whitfield, 1974). The stoichiometric association constant  $K^*$  is defined by Dyrssen et al. as follows:

$$K^* = [\text{MCO}_3] / [\text{M}^{2+}] [\text{CO}_3^{2-}] \quad (1)$$

where brackets designate concentrations. This constant is a measure of the degree of carbonate complexation with the metal ions. If one assumes that  $K^*$  is independent of composition and ionic strength, one can use the constant to estimate the increase in carbonate-metal ion-pair formation,  $\text{MCO}_3$ , and hence estimate the change in the value of  $K'_2$  as a result of the increase in the concentration of calcium and magnesium. Unfortunately, however, the basic assumption — that  $K^*$  is independent of composition and ionic strength — is wrong. This can be readily seen by redefining the constant in a more explicit form (Ben-Yaakov and Goldhaber, 1973; Whitfield, 1975):

$$K^* = (\text{MCO}_3) \gamma_{\text{M}^{2+}} \gamma_{\text{CO}_3^{2-}} / (\text{M}^{2+}) (\text{CO}_3^{2-}) \gamma_{\text{MCO}_3} \quad (2)$$

where parentheses designate activities and  $\gamma$  activity coefficients\*.

Hence, the stoichiometric association constant  $K^*$  and the thermodynamic association constant  $K$  (defined on the generally accepted infinite-dilution

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\* A more rigorous treatment should distinguish between "free" and "total" species. However, the more explicit treatment will not alter the conclusions arrived at here.

activity scale) are related through the equation (Whitfield 1974):

$$K^* = K\gamma_{M^{2+}}\gamma_{CO_3^{2-}}/\gamma_{MCO_3} \quad (3)$$

It is thus obvious that  $K^*$  in DSW can be assumed to be equal to its value in SW only if the activity coefficient has the same value in both waters. Considering the very large differences in ionic composition and ionic strength between DSW and SW, this assumption is probably wrong. Indeed, the study by Garrels (1967) clearly points out that  $\gamma_{M^{2+}}$  for DSW is about 2.5 times larger than its value at the ionic strength (ca. 0.7) of SW. Estimation of  $\gamma_{M^{2+}}$  by the ionic hydration theory (Bates et al., 1970) would predict even larger changes in  $\gamma_{M^{2+}}$  at high ionic strength. According to Bates et al. (1970)  $\gamma_{M^{2+}}$  of ionic strength of 2 is about four times larger than its value at the ionic strength of SW. The ratio is expected to be larger at higher ionic strengths (the ionic strength of DSW is about 8). Unfortunately, our present knowledge is insufficient for accurate calculations of single ion activity coefficients of mixed electrolytes at high ionic strength. At any rate, it would be highly speculative to assume that  $K^*$  in DSW has the same value as in SW. It follows, therefore, that any attempt to estimate  $K_2'$ , without considering the variation in activity coefficient, is rather meaningless.

### (3) *The scatter in the ratio A/C*

The variation of the A/C ratio calculated from our reported results for diluted samples (Sass and Ben-Yaakov, 1977) is taken by Dyrssen et al. as a lack of precision in our experimental procedure. It would appear that they have missed the explicit statement made in our paper (p. 186 in Sass and Ben-Yaakov, 1977): "No special effort was made in order to duplicate exact total dissolved solid (TDS), alkalinity and total dissolved carbon." Upon dilution with distilled water (which may have had a non-zero concentration of  $CO_2$ ) the natural and synthetic samples could have exchanged  $CO_2$  with the atmosphere during handling. Hence, there is no reason why the A/C ratio, calculated from the results reported for the diluted samples, should be equal to the A/C ratios of the original samples. However, the variation in the A/C ratio does not in any way affect the accuracy of  $pK_1'$  and  $pK_2'$  reported by us, since the determination of the constants is independent of A or C in the titrated sample.

### (4) *Similarity to Gran function*

Dyrssen et al. correctly point out that the equation used by us to derive alkalinity (eq. 14, Sass and Ben-Yaakov, 1977) is basically the Gran function. However, eq. 14 was shown by us to be but a special case of the general titration function (eq. 13, op. cit.) which was used to derive the apparent dissociation constants.

(5)  $p(K_2'/K_1')$  scatter

The scatter in the  $K_2'/K_1'$  ratios calculated from our results (Sass and Ben-Yaakov, 1977) is taken by Dyrssen et al. as evidence for lack of precision of our experimental and analytical procedures. They further suggest that their experimental and computational methods are more accurate as they produce a smaller scatter in the  $K_2^*/K_1^*$  ratio. It turns out, however, that the comparison between the scatter of two sets of results is *meaningless*. Our results are given for a number of different natural and synthetic Dead Sea waters. As already pointed out, the ionic composition of DSW is not constant and hence one would not expect to obtain constant  $K_2'/K_1'$  ratios. On the other hand the results reported by Dyrssen et al. are for repeated titrations on the same synthetic DSW sample.

Hence, whereas the scatter in their results reflects only the analytical non-reproducibility, the scatter in our results also indicates the expected variability of the apparent constants in natural and synthetic DSW. Our conclusions were based on the general trend in the magnitude of the constants (fig.6 in Sass and Ben-Yaakov, 1977) and not on the exact values of the constants. Furthermore, we do not believe that a meticulous determination of the apparent constants in DSW is warranted considering the variability in the ionic composition.

(6) *Curve fitting methods*

Dyrssen et al. suggest that the curve-fitting method used by us (Sass and Ben-Yaakov, 1977) to derive  $pK_1'$ ,  $pK_2'$  and  $C$  does not work properly and that the iteration used by them is "more natural". This conclusion is drawn from the fact that  $K_2'/K_1'$  calculated from our results is about twice as large as  $K_2^*/K_1^*$  as determined by Dyrssen et al. Since they assume that their values are accurate, it follows that our values for  $K_1'$  and  $K_2'$  must be inaccurate.

The calculation method used by Dyrssen et al. to derive  $K_1^*$ ,  $K_2^*$  and  $C$  is a direct, non-linear least-square fitting procedure in which the data points are fitted to the titration equation. We chose to transform the titration equation into a linear form and then use a linear least-square fitting procedure. There is, of course, no *a priori* advantage of one approach over the other, but our procedure has a practical advantage; the calculation can be carried out on any small desk calculator using standard linear least-square fitting programs.

Whatever the least-square method procedure used, one *must* check his results against an independent method to verify the validity of the derived parameters. This is important not only for checking the proper operation of the iteration program but also to avoid the possibility of an erroneous fit. That is, a good fit cannot, by itself, be taken as a proof of the physico-chemical validity of the derived coefficients, even if one assumes that the computer program is without a flaw.

As thoroughly discussed (Sass and Ben-Yaakov, 1977), the values of  $pK'_1$  and  $pK'_2$  which were derived by us by fitting the HCl titration data to a model equation, were checked against an independent determination of  $pK'_{12}$  which is defined as the arithmetic mean of  $pK'_1$  and  $pK'_2$ . The value of  $pK'_{12}$  was determined by  $\text{NaHCO}_3$  titration and its value was found to agree well with value calculated from  $pK'_1$  and  $pK'_2$  as determined by the HCl titration. The largest deviation between the two independent determinations of  $pK'_{12}$  (carried out on four different samples) was only 0.1 unit.

Dyrssen et al. apparently did not find it necessary to check their results for  $K_1^*$  and  $K_2^*$  against an independent method. Acidification, boiling and uptake of  $\text{CO}_2$  in a solution of NaOH or  $\text{Ba}(\text{OH})_2$  could have been used to independently determine C. An IR determination of  $\text{CO}_2$  could also have been used.

It should be re-emphasized that our aim was not to determine  $K'_1$  and  $K'_2$  with the utmost accuracy since we believe that there is little merit in doing this. As stated above, the ionic composition of DSW is variable and a very precise determination of the constants for one particular composition seems futile.

It appears then that the statement made by Dyrssen et al. that the iteration process used by us for deriving  $pK'_1$ ,  $pK'_2$  and C "does not work properly" is rather presumptuous as no acceptable evidence is produced to support it.

#### (7) *Ionic medium activity scales*

Dyrssen et al. suggest that there is yet another source of error in our experimental procedure: the use of standard (low ionic strength) pH buffers. This, according to Dyrssen et al. introduces "an unknown liquid junction potential and poorly defined activity scales for  $\text{H}^+$ ". This statement leaves the impression that the approach favored by Dyrssen and co-workers (ionic medium activity scales) is a sort of "instant cure" to the liquid junction potential problem that is common to all specific ion-electrode studies. We disagree. As will be discussed below, there is no evidence that application of medium activity scales to DSW studies are in any way better from the theoretical or experimental point of view than application of the conventional infinite dilution activity scales. In fact, it is our opinion that application of the medium activity scales to the study of non-standard solutions such as DSW, introduces unnecessary practical complications.

Professor Sillén (1967) advocated the use of ionic medium activity scales in chemical oceanography. The approach is of course entirely legitimate from a thermodynamic point of view. Rather than arbitrarily assigning a value of 1 to the activity coefficient at infinite dilution, one can make this arbitrary assignment for any chosen solution. Since seawaters have a constant composition throughout the world oceans, Sillén (1967) proposed to use standard seawater as the standard state in chemical oceanography studies. This

approach has been adopted by Dyrssen and co-workers (Dyrssen and Hansson, 1973; Hansson, 1973). They defined the first and second dissociation constants of carbonic acid in seawater as:

$$K_1^* = [\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3] \quad (4)$$

and:

$$K_2^* = [\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3] \quad (5)$$

where brackets designate concentration. It is beyond the scope of this note to assess the advantage of using the ionic medium scales in chemical oceanography. It would be sufficient to point out that we agree with the evaluation of Pytkowicz and Kester (1971): "The Dyrssen—Sillén constants only differ from apparent constants in the use of  $|\text{H}^+|_T$  instead of  $a_{\text{H}}$ . This difference is not important from a practical point of view." However, we are obliged to refute the notion that the apparent dissociation constants  $K_1'$  and  $K_2'$  (Lyman, 1956) are more prone to errors due to liquid junction potential than the constants  $K_1^*$  and  $K_2^*$  which are based on the ionic medium activity scale.

On the surface, it seems as if the determination of  $K_1^*$  and  $K_2^*$  does not involve the liquid junction potential, and hence is free of the problem. As discussed by Dyrssen et al. all measurements are made on the same solution, including the calibration of the glass electrode which is done after excess acid is added. However, a closer examination of the technique will reveal that it relies on a basic underlying assumption concerning the liquid junction potential. Measurements are made with a pH electrode pair, a glass electrode and a reference electrode. Hence, the precision of the measurement is limited by the reproducibility of the pH electrode, similarly to the case when the apparent constants system is used. Furthermore, it is implicitly assumed that the liquid junction potential is maintained constant during the measurement. For if the liquid junction is unstable or drifts as a function of time it would introduce an equivalent error in the potential measurement. Now, this exactly same assumption — the stability of the liquid junction potential during the measurement — is the primary assumption made (as far as the liquid junction potential is concerned) when determining the apparent dissociation constants. Admittedly, the values of  $K_1'$  and  $K_2'$  determined in this way are dependent on the magnitude of the liquid junction potential in DSW. But as long as one assumes that the liquid junction potential is stable in DSW and in the standard buffers used,  $K_1'$  and  $K_2'$  are truly constants of the system and carry no less information than  $K_1^*$  and  $K_2^*$ . Therefore, one gains no advantage by working with the stoichiometric constants rather than with the apparent constants. For the same reasons, determination of pH in hypersaline solutions by the conventional method using the practical pH scale (Bates, 1956) is entirely valid, although the pH values so determined may not be an accurate measure of  $\text{H}^+$  activity in the solution (Bates, 1969). This discrepancy is due to the liquid junction potential. But then, no other

experimental method is known for a more accurate determination of the activity of  $H^+$  in solution. The method of the ionic medium activity scale, that is, arbitrarily defining the solution as the standard state and hence assigning the value of 1 to the activity coefficient, really solves nothing. On the other hand, in many cases small uncertainties in the values of the activity of  $H^+$  are acceptable. For example, many biological systems tolerate small variations in pH. Here, the practical pH scale has a lot to offer in assisting the investigator to evaluate the vital parameters of the environment.

It is of course the prerogative of every scientist to prefer one model over another when studying natural phenomena; science could only benefit from the diversity. In this respect we firmly believe that the scientific work of Professors Sillén, Dyrssen and co-workers on ionic medium activity scale has contributed significantly to marine chemistry. However, we do not share the opinion that our investigation of DSW (Sass and Ben-Yaakov, 1977) could have benefitted from the use of ionic medium activity scales. It is entirely possible, of course, that the experimental and/or analytical procedures adopted by us in the investigation of DSW (Sass and Ben-Yaakov, 1977) are not free of errors. Future studies will hopefully shed more light on the carbonate chemistry of DSW.

### *Summary*

The ionic medium activity scale has no advantage over conventional approaches when applied in the study of geochemical environments such as DSW. Nor does it circumvent, in any way, the problems associated with the liquid junction potential. Furthermore, extremely useful parameters such as pH (as measured by a glass and reference electrode pair and defined on the practical pH scale) cannot be used within the framework of the ionic medium activity scale.

Although the question of analytical and computational precisions were not major issues in our study (Sass and Ben-Yaakov, 1977) no acceptable evidence is put forward by Dyrssen et al. (1978, this issue, pp. 275–279) to support the claim that their methods are more accurate, or prove the conjecture that our results are in error.

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