

RELATIONSHIP BETWEEN $\Phi\left(\frac{z}{l}, \chi\right)$ RULE OF CHEMICAL PROCESSES IN SEAWATER AND HSAB PRINCIPLE

—PRINCIPLE OF LEAST Σ AND CHEMICAL
MODEL OF SEAWATER

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ABSTRACT

This article reports on the application of the $\Phi\left(\frac{z}{l}, \chi\right)$ rule of chemical processes in seawater to the study of the Principle of Hard and Soft Acids and Bases (HSAB). One result is the establishment of new scales of the hardness-softness of acids and bases which are more complete than those in the literature.

Based on the principle of HSAB as well as abundant experimental data, we developed a new general principle of marine chemistry viz. the principle of least Σ . Application of the principle of least Σ has produced good results in the study of chemical model of the major constituents of seawater, the chemical speciation of trace elements, inorganic ion exchange reactions, the Irving-Williams series of transition elements, etc. Our investigations indicate that chemical models of the major constituents of seawater should take into consideration the formation of chloride ion pairs.

I. NEW QUANTITATIVE SCALE OF HARDNESS-SOFTNESS OF ACID AND BASE

The core of the subject studied in connection with HSAB is the hardness-softness classification of metallic ions and ligands as well as the quantitative scale of hardness-softness of acids and bases. In this connection researchers abroad and in this country have done much work^[2-6], but the results of their achievements are divergent.

In this article, we use the $\Phi\left(\frac{z}{l}, \chi\right)$ rule of chemical processes in seawater to establish quantitative scales of the hardness-softness of acids and bases on the basis of: (i) further analyses of the mutual interactions between broad-sense acids and bases^[7,8], and (ii) the application of the $\Phi\left(\frac{z}{l}, \chi\right)$ rule to hydration energy, solubility, potential, etc.^[9a-9f]

The analyses we made of the mutual interactions between broad-sense acids and bases can be roughly classified as follows: (i) electrostatic interaction (including ionic polarization), (ii) formation of σ -bonds and π -bonds between covalent acceptors and donors, and (iii) formation of feedback π -bonds from acid to base. The $\phi\left(\frac{z}{l}, \chi\right)$ rule uses ionic potential $\left(\frac{z}{l} \text{ or } \frac{z}{r}\right)$ and electronegativity (χ) as the two major parameters in the study of chemical processes occurring in seawater. $\frac{z}{l}$ and $\frac{z}{r}$ reflect mainly the electrostatic effect, that is, the interaction between two charged ions, which can be taken as an indication of the ability of an atom or an ion to form an ionic bond. Electronegativity is "the power of an atom in a molecule to attract electrons itself" (Pauling, 1959). Or according to Mulliken electronegativity is determined by the sum of atomic ionization energy and electronic affinity, is related to the power of a molecule to attract or expel electrons, and can be considered as a measurement of an atom or an ion to form covalent bonds (included σ -bonds, π -bonds, and feedback π -bonds). Therefore, the $\phi\left(\frac{z}{l}, \chi\right)$ rule reflects the above-mentioned interactions between acids and bases in a broad sense. It is hoped that the design of function $\phi\left(\frac{z}{l}, \chi\right)$, composed of these two parameters, might give results which agree with experimental results.

We have shown^[9a-10] that the application of the $\phi\left(\frac{z}{l}, \chi\right)$ rule to hydration energy, solubility, electrochemical potential of metals, etc. has been successful. Relationships of electronegativity with electron affinity and ionization energy and the relationship of $\frac{z}{r}$ with the radius or ionic charge are all so obvious as to necessitate no further discussion. Klopman's formula for E_n^\pm and E_m^\pm relates E_n and E_m to ionization energy and electronic affinity, and energy of desolvation E_d , to the electron density of the frontier orbital's ionic radius and ionic density. Therefore, function ϕ coincides with E_n^\pm and E_m^\pm . For the same reason, the $\phi\left(\frac{z}{l}, \chi\right)$ rule also corresponds to Misono's y and Ahrlund's σ_A and σ_B . Figs. 2—6 show the correlatographs of $\phi_A-E_n^\pm$, ϕ_A- , $\phi_A-\sigma_A$, $\phi_B-E_m^\pm$, and $\phi_B-\sigma_B$. These relationships are linear and thus qualitatively show the general agreement between our results and the literature approaches.

In Fig. 1, we plotted the HSAB relationship graph for $\left|\frac{z}{r}\right|-\chi$ in light of Pearson's HSAB classification table, as we have done earlier^[9a-9f,10] with $\left|\frac{z}{r}\right|$ as the ordinate and χ as the abscissa. There is clearly a boundary between hard and soft acids, hard acids located above the upper left part of the line and soft acids below the lower right part, while intermediate acids are scattered on or near the borderline. The equation of the borderline (1) is:

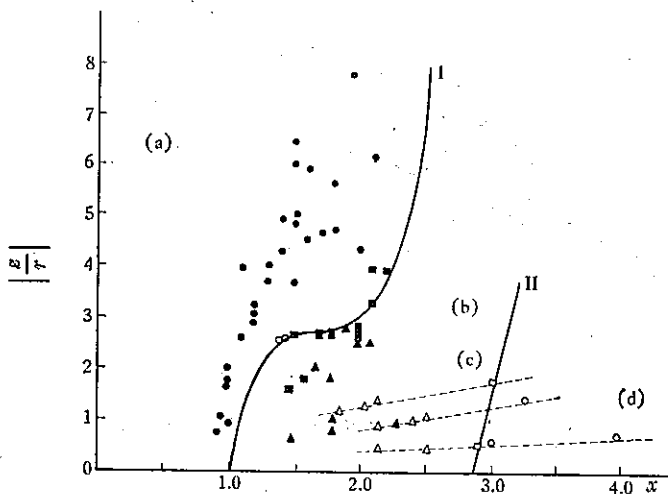


Fig. 1. The distribution of hard and soft acid and bases versus $\frac{z}{r}$ and χ . The open circles, triangles and squares represent the hard, soft and intermediate acid respectively; the closed circles, triangles and squares represent, respectively, the hard, soft and intermediate bases.

$$\frac{z}{r} - 8.00(\chi_A - 1.70)^3 - 2.70 = 0.$$

So the function Φ_A , the quantitative scale of the hardness-softness of acids is expressed as:

$$\Phi_A = \frac{z}{r} - 8.00(\Phi_A - 1.70)^3 - 2.70.$$

On the basis of the Φ_A value, a qualitative classification of hard and soft acids can be made, e. g. hard acids— $\Phi_A > 0.64$, soft acids— $\Phi_A < -0.50$, and intermediate acids— $-0.50 < \Phi_A < 0.64$. A quantitative comparison of the hardness-softness of acids is also possible on the basis of function Φ_A . Using the values of z , r , or χ , etc., which have already been obtained, we calculated the Φ_A values of the acids of 106 cations. They are listed in Table I in order of increasing Φ values. The parameter values of acid hardness-softness of Yingst, Misono, and Klopman and Ahrland's $\frac{\alpha}{\beta}$, Y , E_n^\ddagger , and σ_A have also been listed for comparison. The values from the Φ_A scale agree well with those from Pearson's classification table, except for Sn^{2+} and Pb^{2+} , which disagree slightly. The results presented in Table I are clearly better than those obtained by our predecessors (Yingst and McDinied, 1967; Misono *et al.*, 1967; Klopman, 1968; Ahrland, 1968a,b; Pearson, 1973; Liu, 1976) or those reported in the literature.

Graphs plotting our Φ_A values against our predecessor's E_n^\ddagger , Y , and σ_A values (Figs. 2-4) show that $\Phi_A - E_n^\ddagger$, $\Phi_A - Y$, and $\Phi_A - \sigma_A$ correlate largely linearly. The out-of-line points vary from graph to graph, but our linear relationships have a better

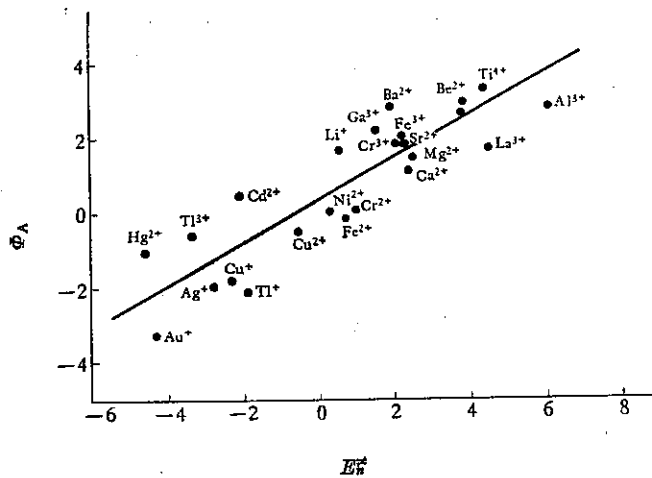


Fig. 2. The correlation of Φ_A versus E_m^0 for acids.

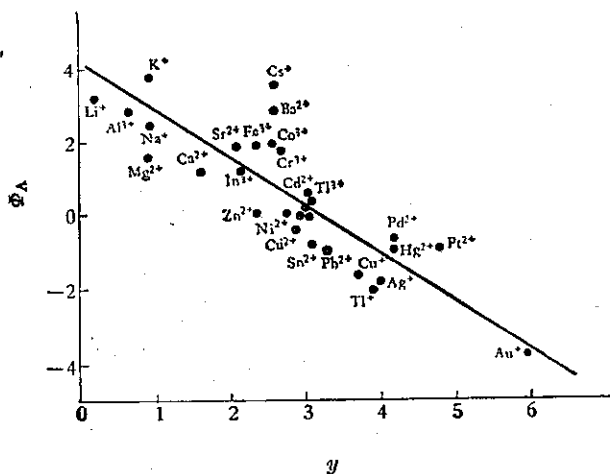


Fig. 3. The correlation of Φ_A versus y for acids.

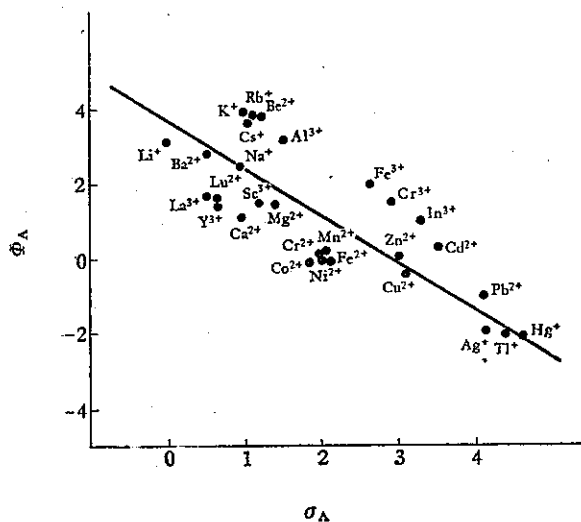


Fig. 4. The correlation of Φ_A versus σ_A for acids.

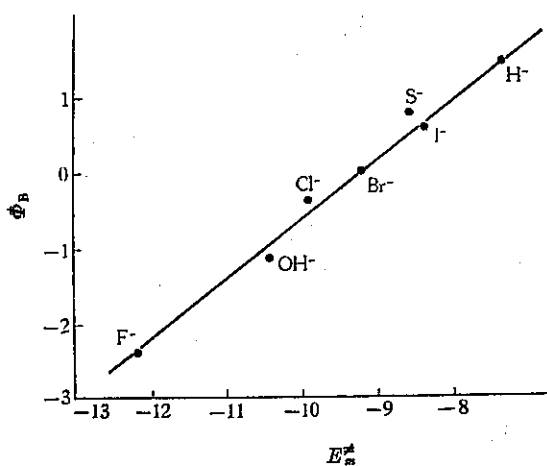


Fig. 5. The correlation of Φ_B versus E_m^0 for bases.

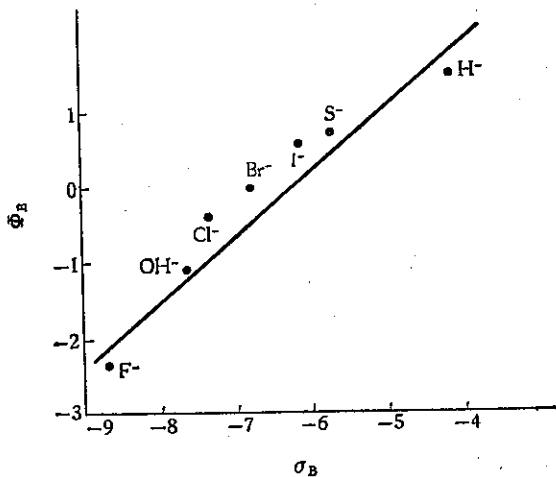


Fig. 6. The correlation of Φ_B versus σ_B for bases.

fit than those for $E_n^\pm - Y$, $E_n^\pm - \sigma_A$, and $Y - \sigma_A$, so the variation probably is not caused by our Φ_A values.

As for base donors, electronegativity χ data are lacking and consequently reliability is poor, so only the relationship of $\frac{z}{r}$ against χ of common simple ionic bases is shown in Fig. 1. A comparison with Pearson's classification table^[5] shows that there is also a clear borderline between hard and soft bases. Soft bases occupy the area above and left of the borderline and hard bases the area below and right of the line—the exact opposite situation from acids. Intermediate bases, like intermediate acids, are located on or near the borderline:

$$\left| \frac{z}{3r} \right| - 2.10\chi_B + 5.70 = 0,$$

so the function Φ_B , the quantitative scale of the hardness-softness of bases is expressed as:

$$\Phi_B = \left| \frac{z}{3r} \right| - 2.10\chi_B + 5.70. \quad (2)$$

As with Φ_A , a qualitative classification of hard and soft bases can be made, e. g. hard bases— $\Phi_B < 0$, soft bases— $\Phi_B > 0$, and intermediate bases— $\Phi_B \approx 0$. Not only is this scale in qualitative agreement with Pearson's classification table, but it also quantitatively parallels Klopman's E_m^\pm (1968)^[3] and Ahrland's σ_B (1968)^[4], both of which are softness parameters of bases (see Table 2). Correlations of $\Phi_B - E_m$ and $\Phi_B - \sigma_B$ (Figs. 5-6) show a good linear relationship. Therefore, Φ_B and E_m and Φ_B and σ_B are interconvertible.

II. THE PRINCIPLE OF LEAST Σ

On the basis of the HSAB principle (viz. hard acids readily bond with hard bases and soft acids readily bond with soft bases, but hard acids are disinclined to bond with soft bases) and the Φ scale, as well as chemical models of the speciation of elements in seawater, we found that two factors largely control the interactions between hard and soft acids and bases in seawater. The first factor may be called the "principle of least σ " and the second factor concerns the concentration of the elements.

The principle of least σ is actually a restatement of the HSAB principle. If Φ_A and Φ_B are numerical values of the hardness-softness of acid acceptor A and base donor B, the intensity of the reaction between A and B can be expressed as the sum of these Φ values, or σ . Consider, for example, a seawater system in which A reacts with B_1, B_2, \dots, B_n . When B_1, B_2, \dots, B_n have the same concentration, then, generally speaking, the A-B pair with the lowest σ value has the strongest interaction and the most stable binding force.

These two factors may be summed up by the principle of least Σ . The A-B pair which has the strongest reaction and the most stable bond has the lowest Σ value. The mathematical expression of Σ is:

$$\Sigma = |\sigma| + \alpha pX, \quad (1)$$

Table 1
A New Scale of Hardness-Softness of Acid, Φ_A

Cations		z/r	χ_A	Φ_A	$\sigma_A^{(a)}$	$\left \frac{\alpha}{\beta} \right ^{(b)}$	$Y^{(c)}$	$E_n^{(d)}$
Soft acid	Au ⁺	0.91	2.3	-3.53	—	—	5.95	-4.35
	Tl ⁺	0.63	1.5	-2.01	—	—	3.78	-1.88
	In ⁺	0.71	1.5	-1.93	—	—	—	—
	Ag ⁺	0.79	1.8	-1.92	4.1	16.5	3.99	-2.82
	Hg ⁺	0.79	1.8	-1.92	4.6	—	—	—
	Cu ⁺	1.04	1.8	-1.67	—	28.4	3.45	-2.30
	Ir ⁺	2.20	2.1	-1.01	—	—	—	—
	Pb ²⁺	1.57	1.4	-1.00	4.1	—	3.17	—
	Hg ²⁺	1.82	1.9	-0.94	—	18.7	4.24	-4.64
	Sn ²⁺	1.82	1.6	-0.88	—	—	3.17	—
	Pt ²⁺	2.50	2.1	-0.71	—	—	4.82	—
	Pd ²⁺	2.50	2.1	-0.71	—	—	4.27	—
	Cd ²⁺	2.06	1.7	-0.64	3.5	12.5	3.04	-2.04
Intermediate acid	Os ²⁺	2.28	1.9	-0.48	—	—	—	—
	Ru ²⁺	2.47	2.0	-0.48	—	—	—	—
	Cu ²⁺	2.50	2.0	-0.40	3.1	9.7	2.89	-0.55
	Ir ²⁺	3.75	2.2	-0.05	—	—	—	—
	Zn ²⁺	2.70	1.8	-0.01	3.1	5.4	2.34	—
	Ni ²⁺	2.70	1.8	-0.01	2.0	—	3.82	0.29
	Co ²⁺	2.74	1.8	-0.01	1.8	—	2.96	—
	Fe ²⁺	2.70	1.7	0.00	2.1	—	3.09	0.69
	Sb ³⁺	3.26	2.1	0.06	—	—	—	—
	Bi ³⁺	2.78	1.8	0.08	—	—	—	—
	Cr ³⁺	2.56	1.4	0.08	2.0	—	—	0.91
	Mn ²⁺	2.56	1.4	0.08	2.0	8.7	3.03	—
	Tl ³⁺	3.16	1.9	0.40	—	—	3.23	-3.37
Rh ³⁺	3.85	2.1	0.64	—	—	—	—	
Hard acid	Pu ³⁺	3.00	1.3	0.81	—	—	—	—
	Am ³⁺	3.03	1.3	0.84	—	—	—	—
	Nd ³⁺	2.73	1.2	1.03	—	—	—	—
	Ca ²⁺	2.02	1.1	1.05	0.9	3.5	1.62	2.33
	Pm ³⁺	2.78	1.2	1.03	—	—	—	—
	Eu ³⁺	2.86	1.2	1.16	—	—	—	—
	Gd ³⁺	2.91	1.2	1.21	—	—	—	—
	U ²⁺	2.91	1.2	1.21	—	—	—	—
	In ³⁺	3.70	1.5	1.22	3.3	6.9	2.24	—
	Tb ³⁺	2.97	1.2	1.27	—	—	—	—
	Dy ³⁺	3.00	1.2	1.30	—	—	—	—
	Ho ³⁺	3.03	1.2	1.33	—	—	—	—
	Er ³⁺	3.06	1.2	1.36	—	—	—	—
	Mg ²⁺	3.08	1.2	1.38	1.4	5.8	0.87	2.42
	As ³⁺	4.35	2.0	1.43	—	—	—	—
	Sc ³⁺	3.70	1.3	1.51	1.2	—	—	—
	Lu ³⁺	3.23	1.2	1.53	0.6	—	—	—
Y ³⁺	3.23	1.2	1.53	0.6	—	—	—	

(to be continued)

(continued)

Cations		z/r	χ_A	Φ_A	$\sigma_A^{(a)}$	$\left \frac{\alpha}{\beta}\right ^{(b)}$	$\Upsilon^{(c)}$	$E_n^{(d)}$
	Th ⁴⁺	4.03	1.4	1.56	—	—	—	—
	La ³⁺	2.61	1.1	1.64	0.5	—	—	4.51
	Ce ³⁺	2.63	1.1	1.66	—	—	—	—
	Pr ³⁺	2.68	1.1	1.71	—	—	—	—
	Sr ²⁺	1.77	1.0	1.81	0.6	13.0	2.08	2.21
	U ⁴⁺	4.30	1.4	1.82	—	—	—	—
	Sm ³⁺	2.80	1.1	1.83	—	—	—	—
	Cr ³⁺	4.55	1.6	1.85	2.9	—	2.70	2.06
	Mn ³⁺	4.55	1.5	1.91	—	—	—	—
	Co ³⁺	4.62	1.7	1.92	—	—	2.56	—
	Fe ³⁺	4.68	1.8	1.97	2.73	3.7	2.37	2.22
	Np ³⁺	2.97	1.1	2.00	—	—	—	—
	Ti ³⁺	4.69	1.6	2.00	—	—	—	—
	Pb ⁴⁺	4.77	1.8	2.06	—	—	—	—
	V ³⁺	4.62	1.4	2.14	—	—	—	—
	Tu ³⁺	3.13	1.1	2.16	—	—	—	—
	Ga ³⁺	4.84	1.5	2.20	—	5.0	—	1.45
	Hf ⁴⁺	4.94	1.4	2.44	—	—	—	—
	Na ⁺	1.05	0.85	2.44	0.93	—	0.93	—
	Pd ⁴⁺	5.41	2.0	2.49	—	—	—	—
	Ir ⁴⁺	5.89	2.1	2.68	—	—	—	—
	Zr ⁴⁺	5.50	1.5	2.74	—	—	—	—
Hard acid	Pa ⁵⁺	5.55	1.7	2.85	—	—	—	—
	Ba ²⁺	1.48	0.9	2.87	0.5	4.4	2.62	1.89
	Os ⁴⁺	5.80	2.0	2.88	—	—	—	—
	Sn ⁴⁺	5.64	1.8	2.93	—	—	—	—
	Pt ⁴⁺	6.15	2.1	2.94	—	—	—	—
	Rh ⁴⁺	6.16	2.1	2.95	—	—	—	—
	K ⁺	0.75	0.8	2.96	1.0	—	0.92	—
	Ce ⁴⁺	3.96	1.1	2.99	—	—	—	—
	Li ⁺	1.67	0.9	3.06	-0.01	—	0.36	0.49
	Ru ⁴⁺	5.96	2.0	3.14	—	—	—	—
	Yb ³⁺	3.16	1.1	3.19	—	—	—	—
	Tl ⁴⁺	5.90	1.6	3.27	—	—	—	—
	Al ³⁺	6.00	1.5	3.36	1.6	0.6	0.70	6.01
	Cs ⁺	0.59	0.75	3.72	1.02	—	2.73	—
	Rb ⁺	0.68	0.8	3.81	1.06	—	—	—
	Be ²⁺	6.45	1.5	3.81	1.2	—	—	3.75
	Bi ⁵⁺	6.76	1.8	4.07	—	—	—	—
	Ta ⁵⁺	7.04	1.7	4.34	—	—	—	—
	Nb ⁵⁺	7.14	1.7	4.44	—	—	—	—
	U ⁶⁺	7.23	1.9	4.47	—	—	—	—
Ge ⁴⁺	7.55	1.8	4.84	—	—	—	—	
Sb ⁵⁺	8.07	2.1	4.86	—	—	—	—	
V ⁵⁺	8.48	1.9	5.72	—	—	—	—	
W ⁶⁺	8.70	2.0	5.78	—	—	—	—	

(to be continued)

(continued)

Cations		z/r	χ_A	Φ_A	$\sigma_A^{a)}$	$\left \frac{\alpha}{\beta}\right ^{b)}$	$Y^c)$	$E_r^{d)}$
Hard acid	Mn ⁴⁺	8.00	2.1	5.81	—	—	—	—
	Mo ⁴⁺	9.68	2.1	6.45	—	—	—	—
	Si ⁴⁺	9.77	1.8	7.04	—	—	—	—
	I ⁷⁺	14.00	2.5	7.21	—	—	—	—
	Te ⁶⁺	10.70	2.1	7.49	—	—	—	—
	As ⁵⁺	10.6	2.0	7.68	—	—	—	—
	Cr ⁶⁺	11.5	2.2	7.80	—	—	—	—
	Re ⁷⁺	12.3	2.2	8.60	—	—	—	—
	Se ⁶⁺	14.3	2.4	9.22	—	—	—	—
	Cl ⁷⁺	26.9	3.0	9.40	—	—	—	—
	Mn ⁷⁺	15.2	1.5	11.65	—	—	—	—
	B ³⁺	15.0	2.0	12.08	—	—	—	—
	C ⁴⁺	26.7	2.5	19.91	—	—	—	—
UO ₂ ²⁺	1.0	1.0	1.00	—	—	—	—	
H ⁺	—	—	1.00	—	—	—	—	

a) Ahrlund, 1968a, b^[4]. b) Yingst and McDiard, 1967^[11].
 c) Misono et al., 1967; Misono and Saito, 1970^[2]. d) Klopman, 1968^[4].

Table 2

A New Scale of Hardness-Softness of Bases, Φ_B

Ion	$\left \frac{z}{r}\right $	χ	Φ_B	$E_m^{a)}$	$\sigma_B^{b)}$
Sb ³⁻	1.23	1.8	2.33	—	—
As ³⁻	1.35	2.0	1.95	—	—
P ³⁻	1.42	2.1	1.76	—	—
Te ²⁻	0.91	2.1	1.59	—	—
H ⁻	0.48	2.1	1.45	-7.37	-4.13
Se ²⁻	1.01	2.4	1.00	—	—
S ²⁻	1.09	2.5	0.82	-8.59	-5.80
(SH ⁻)	1.09	2.5	0.82	-8.59	-5.80
I ⁻	0.46	2.5	0.61	-8.31	-6.13
CN ⁻	—	—	—	—	-6.10
Br ⁻	0.51	2.8	0.00 ₃	-9.22	-6.84
N ³⁻	1.75	3.0	0.00 ₇	—	—
Cl ⁻	0.55	3.0	-0.40	-9.94	-7.38
O ²⁻	1.43	3.5	-1.15	-10.45	-7.60
(OH ⁻)	1.43	3.5	-1.15	-10.45	-7.60
B(OH) ₂ ⁻	—	—	-1.40 to -1.50	—	—
CO ₃ ²⁻	—	—	-1.40 to -1.50	—	—
HCO ₃ ⁻	—	—	-1.40 to -1.50	—	—
SO ₄ ²⁻	—	—	-1.40 to -1.50	—	—
H ₂ O	—	—	-1.50	-10.73	—
F ⁻	0.74	—	-2.42	-12.18	-8.70

a) Klopman, 1968^[4]. b) Ahrlund, 1968a, b^[11].

where $\sigma = \Phi_A + \Phi_B$, pX is the negative logarithm of the concentration (mol/l) of acceptor A or donor B, and α is an empirical coefficient related to the concentration of the element under consideration. Our preliminary investigation indicates that α equals one for a major constituent of seawater and for a minor constituent, α equals 0.05.

There is an abundance of examples which prove the validity of the principle of least Σ when applied to the study of chemical models of seawater, the reactions of inorganic ion exchanges in seawater, the concentration ratios of the marine geochemistry of elements, the ratio of elimination, residence time, and so forth. In the next section, we will discuss some examples.

III. CHEMICAL MODELS OF MAJOR ELEMENTS IN SEAWATER

We have previously dealt qualitatively with the chemical models of the major constituents of seawater and their relationship with the HSAB principle^[12]. A qualitative description of the major constituents of seawater based on the Φ values of the HSAB scale (Tables 1 and 2) agrees fairly well with many chemical models of seawater in the literature^[12-16]. This agreement can be summarized as follows: (i) The major ions of seawater, Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , and H^+ , are all hard acids and thus combine mainly with hard bases. Water with the highest concentration of these ions (55.51 mol/l) is a hard base with a high affinity for metallic ions. These hydrated ions are quite weak acids and generally hydrolysis does not occur in the pH ranges of seawater. (ii) In chemical models of seawater, the strongest combinations between positive and negative ions are H^+ binding with OH^- , HCO_3^- , CO_3^{2-} , and $\text{B}(\text{OH})_4^-$. The absolute Φ_A and Φ_B values of these ions are very close, thus the value for σ approaches zero. Ion pairs with a slightly weaker binding strength are H^+ with SO_4^{2-} , Mg^{2+} with OH^- , and CO_3^{2-} with Mg^{2+} or Ca^{2+} , etc. The σ values for these ion pairs are also very small, but are not as close to zero as the σ values for the above-mentioned ion pairs. (iii) Na^+ , K^+ , Mg^{2+} , Ca^{2+} , and Br^- ; Na^+ , K^+ , and HCO_3^- ; CO_3^{2-} and $\text{B}(\text{OH})_4^-$; etc. generally do not form ion pairs because of a relatively large difference between their Φ_A and Φ_B values.

We can now go a step further and discuss chemical models of seawater quantitatively by using the principle of least Σ . Within the complicated systems of seawater, various cations A and anions B have differing degrees of combination strength, but the A — B pairs with relatively smaller Σ values have a comparably greater stability of combination. There are several of these A — B pairs which represent the major forms of existence of the major constituents of seawater. Specific formulae for calculation follow:

$$\left. \begin{aligned} \Sigma &= |\sigma| + pX \\ \sigma &= \Phi_A + \Phi_B \end{aligned} \right\} \quad (2)$$

The Σ values were calculated for major species using the Φ_A or Φ_B listed in Tables 1 and 2 and the following pX values: $p(\text{Na}^+) = 0.32$, $p(\text{K}^+) = 2.00$, $p(\text{Mg}^{2+}) = 1.27$, $p(\text{Ca}^{2+}) = 2.00$, $p(\text{H}_2\text{O}) = -1.74$, $p(\text{Cl}^-) = 0.25$, $p(\text{SO}_4^{2-}) = 1.90$, $p(\text{HCO}_3^-) = 2.80$, $p(\text{CO}_3^{2-}) = 4.58$, $p(\text{B}(\text{OH})_4^-) = 5.33$. These Σ values are listed in Table 3 along with

Table 3
Speciation of Major Constituents of Seawater and Σ

Constituent A of Main Cation of Seawater	Na(I)		K(I)		Mg(II)		Ca(II)		Sr(II)	
	species ^{a)} (%)	Σ	species (%)	Σ	species (%)	Σ	species (%)	Σ	species (%)	Σ
M^{n+}	98 (82.97) ^{b)}	-0.80	98-99 (78.28)	0.28	87-92 (48.14)	-1.62	85-92 (43.54)	-1.29	86	-1.43
MCl^{n-1}	V	V	V	V	V	V	V	V	V	V
	0 (13.31)	2.29	0 (17.45)	2.81	0 (42.71)	1.23	0 (46.90)	0.90	V	1.66
MSO_4^{n-2}	V	V	V	V	V	V	V	V	V	V
	2.24 (3.72)	2.77	1-2 (4.27)	3.29	7.9-12 (9.16)	1.75	7.9-12 (9.53)	2.08	12	2.14
$MHCO_3^{n-1}$	-	V	-	V	0.1-0.5	V	0.06-0.5	V	V	V
	-	3.77	-	4.29	2.75	2.75	3.08	3.08	0.4	3.14
MCO_3^{n-1}	-	V	-	V	0.15	V	0.05	V	-	V
	-	5.59	-	6.11	4.57	4.57	4.90	4.90	-	4.96
$MB(OH)^{n-1}$	-	V	-	V	0.02	V	0.01	V	-	V
	-	6.37	-	6.89	5.35	5.35	5.63	5.63	-	5.74

Constituent B of Main Anion of Seawater	Cl(I)		SO ₄ (II)		CO ₃ (II)		HCO ₃ (I)		B(OH) ₃ (I)	
	species (%)	Σ	species (%)	Σ	species (%)	Σ	species (%)	Σ	species (%)	Σ
X^{n-}	100 (88.31)	-0.64	39-46 (15.93)	-1.74	8-9	-1.67	68-81	-1.71	56-76	-1.64
NaX^{1-n}	V	V	V	V	∥	V	V	V	V	V
	0 (11.34)	2.36	16-40 (61.75)	1.26	3-16	1.33	11-20	1.29	15	1.36
MgX^{2-n}	V	∥	V	V	∧	∧	V	V	∧	∧
	0 (4.14)	2.27	15-22 (17.30)	1.39	44-50	1.32	6-14	1.36	22-24	1.29
CaX^{2-n}	V	V	V	V	V	V	V	V	V	V
	0 (0.88)	2.65	3-5 (3.49)	2.45	21-38	2.38	1.5-3	2.42	7	2.35
KX^{1-n}	V	V	V	V	-	V	V	V	-	V
	0 (0.33)	4.56	0.42 (1.56)	3.46	-	3.30	-	3.49	-	2.56

a) Taken from Chang and Liu, 1974, 1977a, 1977b; Dyrssen and Wedborg, 1974; Kester et al., 1975; Ahrlund, 1975; Stumm and Bauner, 1975.

b) Values in parentheses are taken from Johnson and Pytkowicz, 1979.

percentages of the species of the constituents of seawater. It is also possible to anticipate from the Σ values the order of percentage of various complexes. Except for the M-Cl ion pair, the order of formation of ion pairs predicted from the principle of least Σ (Table 3) is the same as that reported in the literature^[12-16]. As for the M-Cl ion pair, our calculations predict not only the possibility of this pair forming, but also that the percentage of the M-Cl ion pair is greater than that of the M-

SO_4^{2-} ion pair, which agrees with the recent results of Johnson and Pytkowicz (1979, their values are listed in parentheses in Table 3).

The formation of the M-OH ion pair is generally not considered in chemical models, but according to the principle of least Σ the Mg-OH and Ca-OH ion pairs are rather stable and rank only slightly lower than M-B(OH)_4 ion pairs.

Certain complexes of organic ligands and the major constituents of seawater also exist, but because of the low concentrations of organic ligands in seawater, these complexes are omitted from calculation.

IV. CHEMICAL MODELS OF MINOR ELEMENTS IN SEAWATER

As with the major constituents of seawater, we can now go beyond our previous qualitative discussions of the minor elements and the HSAB principle^[12] and deal with them quantitatively using the principle of least Σ . The method of calculation used for the minor elements of seawater is similar to the one used for the major constituents. Table 4 lists the speciation of the minor elements which are generally recognized in the literature^[12-16]. The results from the least Σ principle for the forty elements listed are in good agreement with the results reported in the literature. Also included in Table 4 are the values of $\Phi_{\text{A-OH}}$ and $\Phi_{\text{A-Cl}}$ calculated from the Φ_{A} and Φ_{B} values (Tables 1 and 2) and the pX value from the literature (Table 1)^[17b]. Concrete formula of calculation using principle of least Σ is

$$\left. \begin{aligned} \Sigma &= |\sigma| + 0.05pX \\ \sigma &= \Phi_{\text{A}} + \Phi_{\text{B}} \end{aligned} \right\} \quad (3)$$

The principal inorganic species of the minor elements are divided mainly into two types—free ions and ligand complexes of M-Cl and M-OH. The M-Cl complexes are formed by the cation M of soft and intermediate acids and the ligand Cl, and the M-OH complexes are formed by hard acids and ligand OH.

Table 4 lists $\text{UO}_2(\text{OH})_3^-$ as the main species of uranium in seawater. This disagrees with the literature which generally considers $\text{UO}_2(\text{CO}_3)_3^{4-}$ as the major species, but it does agree with our results from a previous study^[12] as well as experimental results. Calculations based on the principle of least Σ and Eq. (3) give: $\Sigma\text{UO}_2\text{-OH}$ (0.41) < $\Sigma\text{UO}_2\text{-CO}_3$ (0.59) < $\Sigma\text{UO}_2\text{-Cl}$ (0.65). Thus the quantities of uranium species according to the principle of least Σ are: $\text{UO}_2\text{-OH} > \text{UO}_2\text{-CO}_3 > \text{UO}_2\text{-Cl}$. It is possible that a certain percentage of the uranium exists as $\text{UO}_2(\text{CO}_3)_3^{4-}$ even though the major species is $\text{UO}_2(\text{OH})_3^-$. The principle of least Σ also explains why the small quantity of $\text{UO}_2\text{Cl}^{2-}$ may be overlooked.

The principle of least Σ predicts that elements which are soft acids will form complexes with Br. This agrees well with the results of Ahrlund^[16] and Dyrssen and Wedborg^[14] among others who reported the existence of AuCl_nBr (6%), AgCl_nBr ($n = 1, 2,$ and 3), HgCl_nBr ($n = 1, 2,$ and 3 ; HgCl_3Br 12%), and CdCl_nBr (6%). The complexes involve Cl rather than iodine because the species of iodine in seawater are rather complicated—the abilities of IO_3^- and I to bond with metallic ions differ widely—and the quantities of iodine are comparatively small. Thus iodine cannot compete with chlorine.

Table 4

Speciation of Minor Elements of Seawater and Σ (25°C, latm, S = 35‰, pH = 8.1)

Minor Elements	Principal Inorganic Species	Φ_A	Σ_{A-OH}	Σ_{A-Cl}	Types of Bonds Anticipated by Principle of Least Σ
Au ⁺	AuCl ₂	-3.53	4.98	3.94	Au-Cl
Ag ⁺	AgCl _n (n = 4, 3, 2)	-1.92	3.37	2.33	Ag-Cl
Pb ²⁺	PbCl _n (n = 2, 1), PbCO ₃	-1.00	2.45	1.41	Pb-Cl
Hg ²⁺	HgCl _n ²⁻ⁿ (n = 4, 3)	-0.94	2.39	1.35	Hg-Cl
Cd ²⁺	CdCl _n ²⁻ⁿ (n = 2, 1, 3)	-0.64	2.09	1.05	Cd-Cl
Cu ²⁺	CuOHCl	-0.42	1.87	0.83	Cu-Cl
Fe ²⁺	FeCl ⁺ , FeOH ⁺	-0.08	1.46	0.42	Fe-Cl
Co ²⁺	Co ²⁺ , CoCl ⁺	-0.01	1.46	0.42	Co-Cl
Ni ²⁺	Ni ²⁺ , NiCl ⁺	0.03	1.46	0.42	Ni-Cl
Zn ²⁺	Zn ²⁺ , ZnCl ⁺ , Zn(OH) ₂	0.06	1.45	0.41	Zn-Cl
Mn ²⁺	Mn ²⁺ , MnCl ⁺	0.08	1.37	0.33	Mn-Cl
Ce ³⁺		1.66	0.81	1.27	Ce-OH
Pr ³⁺		1.71	0.86	1.32	Pr-OH
Nd ³⁺		1.03	0.42	0.64	Nd-OH
Pm ³⁺		1.08	0.37	0.67	Pm-OH
Sm ³⁺		1.83	0.98	1.44	Sm-OH
Eu ³⁺		1.16	0.31	0.77	Eu-OH
Gd ³⁺	Me(OH) ₅ ³⁻² , Me	1.21	0.36	0.82	Gd-OH
Tb ³⁺		1.27	0.42	0.88	Tb-OH
Dy ³⁺		1.30	0.45	0.91	Dy-OH
Ho ³⁺		1.33	0.48	0.94	Ho-OH
Er ³⁺		1.36	0.51	0.97	Er-OH
Tu ³⁺		2.16	1.31	1.77	Tu-OH
Yb ³⁺		3.19	2.34	2.80	Yb-OH
Lu ³⁺		1.53	0.68	1.14	Lu-OH
UO ₂	UO ₂ (OH) ₅ ⁻ , UO ₂ (CO ₃) ₃ ²⁻	1.04	0.41	0.65	UO ₂ -OH
Se ³⁺	Se(OH) ₃	1.51	0.66	1.12	Se-OH
Y ³⁺	Y(OH) _n ³⁻ⁿ	1.53	0.68	1.14	Y-OH
Th ⁴⁺	Th(OH) _n ⁴⁻ⁿ , Th(CO ₃) _n ⁴⁻²ⁿ	1.56	0.71	1.17	Th-OH
La ³⁺	La(OH) ₃	1.64	0.79	1.25	La-OH
Cr ³⁺	Cr(OH) ₃	1.85	1.00	1.44	Cr-OH
Fe ³⁺	Fe(OH) _n ³⁻ⁿ	1.97	1.12	1.58	Fe-OH
Ga ³⁺	Ga(OH) ₃	2.20	1.35	1.81	Ga-OH
Zr ⁴⁺	Zr(OH) _n ⁴⁻ⁿ	2.74	1.89	2.35	Zr-OH
Sn ⁴⁺	SnO(OH) ₃ ⁻	2.93	2.08	2.54	Sn-OH
Ti ⁴⁺	Ti(OH) ₄	3.27	2.42	2.86	Ti-OH
Al ³⁺	Al(OH) ₃	3.36	2.41	2.97	Al-OH
Be ²⁺	Be(OH) ₂	3.81	2.96	3.42	Be-OH
Ge ⁴⁺	GeO(OH) ₃ ⁻	4.84	3.98	3.45	Ge-OH
Sb ⁵⁺	Sb(OH) ₅ ⁻	4.86	4.01	3.47	Sb-OH
W ⁶⁺	WO ₄ ²⁻	5.78	4.93	5.39	WO ₄ ²⁻
Si ⁴⁺	Si(OH) ₄	7.04	6.19	6.65	Si-OH
Re ⁷⁺	ReO ₄ ⁻	8.60	7.75	8.24	ReO ₄ ⁻
B ³⁺	B(OH) ₃	12.08	11.19	11.65	B-OH

The organic substances which form complexes with metallic ions in seawater are (i) those with low molecular weight in true solutions, (ii) polymeric substances, including a significant number of hydrophilic functional groups ($-\text{COO}^-$, $-\text{RNH}_2$, $-\text{RS}^-$, ROH , RO , etc.), and (iii) colloidal organic materials. For example, polygalacturonic and alginic complexes form with Zn, Cd, Cu, Ni, etc., and humic acid, fulvic acid and Gelbstoffe form complexes with iron, uranium, etc.

We found that organic ligands have an insignificant effect on some trace metals, such as Cd(II), while having considerable effect on others, such as Cu(II). Most organic ligands can form complexes with Mg^{2+} and Ca^{2+} . For instance, the K_1 of Mg^{2+} and Ca^{2+} with glycine is 1000 (M^{-1}) and 10 (M^{-1}) respectively. These observations can be explained by the principle of least Σ . The functional groups of organic substances in seawater are hard bases, so their effect on Cd(II), which is a soft acid, is insignificant. Some of the organic bases, while classified as hard bases, have σ values close to some acids in the intermediate range, so they have a certain effect on some intermediate acids such as Cu(II). On the basis of this analysis, these organic substances should have a strong bonding reaction with hard acids such as iron, uranium(VI), etc., which in fact has been substantiated not only by our laboratory work, but by others' work as well.

V. INORGANIC ION EXCHANGE REACTION IN SEAWATER AND THE PRINCIPLE OF LEAST Σ

1) *Inorganic Ion Exchange Reaction of Trace Elements on Hydrous Titanium Oxide in Seawater*

Hydrous titanium oxide is one of the most often used extractants in the study of uranium extraction from seawater. The capacity for ion exchange reactions of trace elements on hydrous titanium oxide constitutes the crucial question in the theoretical research on uranium extraction and is receiving worldwide attention. [The concentration coefficients of trace elements on hydrous titanium oxide of Keen^[18] and Hideo Wade et al.^[19] are listed below in order of their value.

Keen:	Cr > V > U > Mn > Fe > Ni > Ba > Cu > Al > Si > Sr > Ca > Mg > Na
Hideo et al.:	Cr > Zn > Cu > Fe > Mn > Al > U > Ni > V > As > Ba > Si > Sr > Li > B > Ca > Mg > K

On the whole, the order of these two series is the same with the exception of the transition elements. These discrepancies are understandable considering that the trace elements exist in extremely small quantities in seawater, errors in analysis are rather great, and a great number of factors influence titanium oxide and trace elements.

The principle of least Σ can be applied to all of these experimental results. The Σ values for trace elements are calculated by Eq. (6):

$$\Sigma = |\sigma| + 0.05pX, \quad (6)$$

and the Σ values for the major elements with Eq. (7):

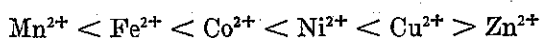
$$\Sigma = 10|\sigma| + pX. \quad (7)$$

The results and Σ values are in the order: Cr (0.88) \simeq U(0.88) $>$ Mn(0.89) $>$ Fe (0.92) $>$ Ni(0.94) \simeq Zn(0.92) $>$ Cu(1.07) $>$ Ba(2.66) $>$ Al(3.17) $>$ Si(6.69) $>$ Ca (6.92) $>$ Mg(9.57) $>$ Na(19.5) $>$ K(28.1).

The order of this series is in close agreement with those of Keen and Hideo Wade. Thus, considering the differences in experimental conditions, the application of the principle of least Σ to this question is successful.

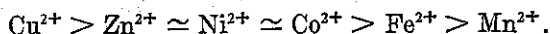
2) Irving-Williams Order of Ion Exchange in Seawater

Rashid^[22] and Mantoura et al.^[23] pointed out that the ion exchange powers of transition elements on humic materials separated from the sediment follow the Irving-Williams order:



with $\text{Ni}^{2+} \simeq \text{Zn}^{2+}$.

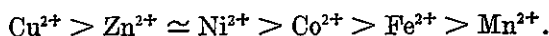
The structure of humic materials is quite complicated as are their reactions with transition elements, but judging from an estimation of their reacting functional groups, they are either hard or intermediate bases. On the basis of the tendency of ion exchange—Mg $<$ Ca $<$ Cd \simeq Mn—the hardness of humic materials is not extremely large, and this is consistent with the structure of humic material. The principle of least Σ can be used to elucidate the Irving-Williams order. The ion exchange powers of transition elements on humic material arranged in order of their Φ_A values from Table 1 are:



Dealing with the transition elements in terms of the parameters $\frac{z}{r}$ and X was not ideal and better results were obtained with the screening loss parameter R_f ^[10]. Known screening loss parameters in order of magnitude are:



The principle of least Σ includes all three factors, Φ_A , pX , and R_f , and predicts the ability of ion exchange of transition elements in the following order:



This agrees with the experimental results of Rashid^[22] and Mantoura et al.^[23]

Takematsu^[24] reported the Kd coefficients of ion exchange of transition elements on clay (Na-montmorillonite) followed the Irving-Williams order. The reaction of transition elements on clay can be expressed by $\text{Me}-(\text{OSi})_n$ because Si^{4+} is a very hard acid. Consequently $-(\text{OSi})_n$ has been classified as a hard base approaching an intermediate base, in the same manner as humic materials, thus the adherence to the Irving-Williams order.

In the same paper, Takematsu^[24] reported the Kd values of transition elements on

inorganic ion exchangers such as hydrous, manganese oxide. According to the γ -MnOOH-manganite- δ -MnO₂ series, these values in order of increasing value are:

Inorganic Ion Exchangers	Kd				
	Mn	Co	Ni	Cu	Zn
γ -MnOOH	3×10^4	5×10^4	1×10^4	8×10^6	2×10^4
7 Å manganite	\wedge	\wedge	\wedge	\parallel	\wedge
	3×10^6	8×10^5	4×10^4	7×10^6	2×10^5
δ -MnO ₂	\wedge	\wedge	\wedge	\wedge	\wedge
	5×10^7	2×10^6	3×10^5	1×10^7	8×10^5

These transition elements are intermediate acids and, according to the principle of least Σ , the bonding strength of Me-B increases as the hardness of B decreases, as long as the concentration (pX) remains the same. In the sequence of γ -MnOOH-manganite- δ -MnO₂, Mn³⁺ become Mn⁴⁺, so the hardness of the base decreases and the Kd value increases. $\Phi_{Mn^{4+}} = 5.81$ and $\Phi_{Si^{4+}} = 7.04$, so these bases are much harder than clay, and thus do not follow the Irving-Williams order when ion exchange occurs with the above transition elements. The order of the three kinds of manganese oxides is irregular. $\Phi_{Ti} = 3.27$, so $(-OTi)$ is harder than $(-OMn)_n$ and $(-OSi)_n$ and an inverse Irving-Williams order may occur when these oxides react with transition elements.

We will not discuss ferric oxide here, since some literature describes it as a hydrate of Fe₂O₃ and elsewhere it is described as hydrous ferric oxide. The literature also disagrees on the order of the ion exchange powers with transition elements. Furthermore, in natural water, its surface electric charge might disagree with the above-mentioned hydrous oxides.

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