chloride analysis of the hydrolysis products in dilute nitric acid-ethyl ether solution.

Infrared spectrograms of the products were obtained using the potassium bromide technique. During the formation of the pellets, some hydrolysis occurred and part of the product formed titanium dioxide and the corresponding phenol. The titanium dioxide gave a broad peak between 2.9 to 3.2μ and a very broad shoulder around 10μ (*1*). Enough of the product remained so that some of the peaks reported by Johannesen and co-workers (*4*) and Kambara (*10*) could be observed. The Ti-Cl bond (*4*) around 10.2μ has been observed as well as the Ti-O-C bond (*10*) found in the 8.5 to 9.5μ wave length range.

A change in the adsorption peaks of the phenol products around 7.5 to 9.1μ was noted. A new peak was formed at 7.75μ. A double peak between 8.0 and 8.5 has been replaced by a single peak at 8.15μ. There is also a formation of new peaks at 8.5 and 8.95μ which are probably due to the Ti-O-C bonds. No bonds were observed around the 10 and 11μ bands because of the TiO_2 present.

The spectrogram of the *o*-bromophenol product showed that there are two new peaks formed at 8.85 and 9.3μ. There were no new peaks observed for the Ti-Cl bond because of the TiO_2 present.

The spectrogram of the *p*-bromophenol showed that a new double peak has formed around 18μ which is not evident in *o*-bromophenol itself. There was no Ti-Cl bond observed because of the TiO_2 present.

The spectrogram of the *p*-chlorophenol product showed that the double peak around 8.0 and 8.5μ has disappeared and a single peak appeared at 8.1μ. A second new peak was observed at 8.55μ. There were no Ti-Cl peaks observed because of the TiO_2 present.

The *p*-nitrophenol did not show any new adsorption peaks formed.

The spectrogram of the β-naphthol product showed a moderately strong peak formed at 8.67μ which may indicate a Ti-O-C bond and another peak formed at 10.23μ which would indicate a Ti-Cl bond.

The spectrogram of the *p*-cresol product showed a very weak peak at 9.35μ which may indicate a Ti-O-C bond.

EXPERIMENTAL

The chemically pure liquid phenols were purified by distillation. The solid phenols were chemically pure and used as such. The titanium tetrachloride was purified by distillation in a dry atmosphere. Reagent grade carbon tetrachloride and chloroform were first dried over calcium sulfate and then distilled.

Infrared analyses were run on the compounds in carbon tetrachloride using the KBr technique on a Beckman IR-5 Double-beam Recording Spectrophotometer.

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Buffer Systems of Natural Fresh Waters

WALTER J. WEBER, Jr., and WERNER STUMM

Department of Water Resources, Division of Engineering and Applied Physics,
Harvard University, Cambridge, Mass.

NATURALLY OCCURRING bodies of fresh water of significant size, such as lakes, rivers, and large streams, are commonly observed to vary but slightly in hydrogen ion concentration, the range of $[H^+]$ generally being $10^{-6.5}$ to $10^{-8.5}$. The relative constancy of pH in a natural water is attributed primarily to the presence in the water of dissolved CO_2, bicarbonate, and carbonate. Since the total concentration of dissolved carbonate species seldom exceeds a few millimoles per liter, however, additional buffering action for the maintenance of nearly neutral pH conditions must be contributed by the numerous other chemical, physical, and biological activities of the waters. Therefore, in addition to a detailed consideration of the role of the carbonate system, a comprehensive, integrated concept of the nature and interplay of the various capacity factors of other principal buffer systems indigenous to fresh waters is presented.

CARBONATE EQUILIBRIA

Prior to the discussion of the modes of action of buffer systems in fresh waters, the equilibria of the carbonate system is considered, and a method is described by which representation of such equilibria may be greatly facilitated. For a simple aqueous solution of carbonate species, the interdependent nature of the equilibrium concentrations of the solute components ($H_2CO_3^*$, HCO_3^-, $CO_3^=$, H^+, and OH^-) can be described completely by five fundamental equations ($H_2CO_3^*$ refers to the sum of CO_2 and H_2CO_3). This system of equations is composed of the three mass law relationships—defining the first and second acidity constants of $H_2CO_3^*$, K_1 and K_2, and the ion product of water, K_w—and any two equations that describe the compositional nature of the solution—e.g., a concentration and an electroneutrality or proton condition.

Simultaneous graphical representation of this system of equations in logarithmic form provides a convenient means for surveying the equilibrium relationships and their respective dependencies upon pH (*1, 7*). Figure 1 is a logarithmic equilibrium diagram for a simple aqueous carbonate system. For the construction of Figure 1, it has been assumed that the total concentration, C_T, of carbonate species is constant at 0.001M, that all activity coefficients are constant, and that the equilibrium constants valid at the appropriate temperature have been corrected for activity. Diagrams such as Figure 1 can be used expediently for

Tha ability of natural fresh waters to maintain a closely constant pH is well recognized, but the interaction of buffer components lending this quality to natural waters is often not clearly defined. Discussion of the relative significance and of the interplay of the principal component systems of such waters is presented in an effort to describe more closely the nature of fresh water buffer capacity. Consideration is given the homogeneous-phase and heterogeneous-phase chemical systems, and the biochemical and physicochemical activities common to most natural fresh waters. Appropriate emphasis is placed upon description of the mode of action of the carbonate system. Conceptual definitions of alkalinity and acidity are presented, and their respective roles in providing buffer action is discussed. Rigorous mathematical expressions for acid-base titrations and buffer capacities in carbonate systems are derived from consideration of conditions of electroneutrality and mass law relationships. A method for simultaneous graphical representation of systems of logarithmic equations treating chemical equilibria is presented as a means for facilitating the survey of equilibrium relationships and their respective dependencies upon control variables such as pH.

evaluating the equilibrium concentrations of the respective species of solute at any pH, or, conversely, for predicting the pH of a solution of specified composition.

BUFFER CAPACITY

The buffer capacity, β, of a water can be expressed in terms of the quantity of strong base, C_B, or the quantity of strong acid, C_A, required to effect a unit change in the pH of the water (*9*). Buffer capacity may then be written:

$$\beta = \frac{dC_B}{d\text{pH}} = -\frac{dC_A}{d\text{pH}} \qquad (1)$$

Relationship to the Titration Curve. Upon titration of a water with strong base or strong acid, a curve relating the pH of the water to the quantity of base or acid added is obtained, the slope of which at any value of pH (seen from Equation 1) represents the buffer capacity of the water at that point in the titration. The titration curve for the addition of strong acid or base to the $10^{-3}M$ carbonate system described earlier has been constructed in Figure 2. The left ordinate represents the equivalent fraction, f, of strong base used to titrate a $10^{-3}M$ solution of $H_2CO_3^*$ and the right ordinate the equivalent fraction, $2 - f$, of strong acid used for the titration of an equimolar carbonate solution. The shape of such a titration curve can be defined rigorously, since at any point in the titration it is requisite that the condition of electroneutrality described in Equation 2 be fulfilled.

$$C_B = [HCO_3^-] + 2[CO_3^{-2}] + [OH^-] - [H^+] \qquad (2)$$

Superposition of the condition of electroneutrality upon the equilibrium relationships described in Figure 1 permits ready deduction of the titration curve shown in Figure 2. The buffer capacity may then be graphically represented as a function of pH by plotting the slopes of the titration curve or by differentiation of the electroneutrality equation with respect to pH (*5*). Figure 3 has been constructed by the latter means for the example used in Figures 1 and 2.

Alkalinity and Acidity. Equation 2 is of general operational and analytical value since for a carbonate system it represents a conceptual definition of alkalinity. Alkalinity may be described as the acid-consuming capacity of an aqueous carbonate system. More rigorously, alkalinity is a measure of the quantity per liter of strong acid required to attain a pH equal to that of a C_T-molar solution of H_2CO_3. Correspondingly, the acidity of an aqueous carbonate solution represents the base-consuming capacity or the quantity of strong base required to attain a pH equal to that of a C_T-molar solution of Na_2CO_3.

Algebraically the alkalinity of a carbonate system can be written as the right-hand side of Equation 2, while acidity is expressed algebraically in Equation 3.

$$[\text{Acidity}] = 2[H_2CO_3^*] + [HCO_3^-] + [H^+] - [OH^-] \qquad (3)$$

It is then obvious from Equations 2 and 3 that

$$[\text{Alkalinity}] + [\text{Acidity}] = 2C_T \qquad (4)$$

The curve representing the buffer capacity of a carbonate system can thus be obtained by differentiation of either the expression for alkalinity or that for acidity, since each of these defines the titration curve for the system (see Equations *A*, *B*, *C*, and *D* in Table I).

The alkalinity for most natural fresh waters having values of pH up to approximately 9 is closely equal to the concentration of dissolved bicarbonate. The buffer capacity, however, as evidenced by Equations *C* and *D* in Table I and by Figure 3, is dependent not only upon C_T but is also an implicit function of pH. Pronounced minima in buffer capacity occur at pH values very close to those of the equivalence points of titration, with exception of that for an f value of 2 (pH for C_T molar Na_2CO_3 solution), as evidenced in Figure 3. The absence of a well defined minimum at an f value of 2 is an example of the role that pH plays in the buffer capacity, since in this range of pH the concentration of hydroxide ions becomes the determining factor in the buffering ability of the solution.

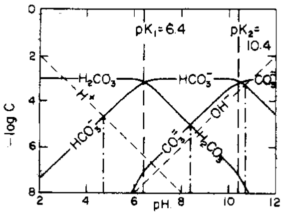

Figure 1. Equilibria for a $10^{-3}M$ carbonate system

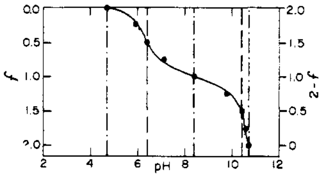

Figure 2. Titration of a $10^{-3}M$ carbonate system with strong acid

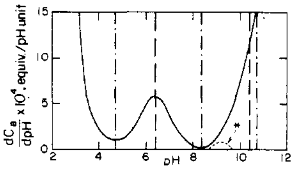

Figure 3. Buffer capacity of a $10^{-3}M$ carbonate system with respect to strong acid

BUFFERING COMPONENTS

Most fresh waters contain in addition to the several carbonate species trace concentrations of other buffering solutes. The total buffer capacity of each water is then very simply the sum of the individual capacity-contributions of the acid-base pairs present. Relatively significant of the buffer components other than carbonates are ammonia, phosphates, and silicates, and occasionally organic acids. Borates play an important role in the buffer capacity of sea water but their presence in sufficiently high concentration to effect a buffering action in fresh waters is rare.

The concentration of each of the above mentioned solutes in fresh water very seldom exceeds $0.0001M$, and, consequently, their respective contribution to the buffer capacity of the over-all system is generally quite small relative to that of the carbonates. For example, the buffer contribution of $0.0001M$ silicate (2.8 mg./liter of Si) in the carbonate system of the original example is shown by the dotted line in Figure 3 to be essentially negligible. Although the proportion of silicate to carbonate species may sometimes be greater than that in Figure 3, the buffer capacity of silicate is a minor factor in the common range of pH of natural water.

Often of greater importance than the aforementioned chemical constituents to the acid-or base-consuming capacity of a fresh water are the many heterogeneous physical, chemical, and biochemical processes occurring in the water. Natural and synthetic processes such as photosynthesis, biological respiration, aeration, erosion and corrosion, chlorination, and metal-ion coagulation tend to influence the acid-base balance of such waters.

The magnitude of the shift in pH resulting from the various chemical, physical, and biological phenomena indigenous to any water is dependent upon the extent of these activities and upon the buffer capacity of that water. Because the buffer capacity controls the magnitude of pH changes in natural waters, it serves as a regulatory factor controlling the rates and extent of the very processes which tend to upset the systemic acid-base balance. For example, it appears that scale deposition and corrosion are considerably dependent upon buffer capacity (*8*).

The Role of Aquatic Biota in Buffer Systems. The steady-state balance between photosynthetic activities—CO_2 assimilation—and heterotropic activities—CO_2 production—represents an important buffering factor in fresh water. Disturbance of this balance may result in wide variation of the pH of the water. For example, nearly exclusive photosynthetic production of CO_2 in the lighted zone of a well fertilized lake, or predominance of bacterial decomposition in the deep layers of a stagnant lake greatly affect pH.

Photosynthesis is also a direct source of dissolved oxygen in natural waters (even atmospheric oxygen generally is assumed to have been produced largely from photosynthesis). Thus, the balance between photosynthetic and oxygen-consuming heterotrophic activities—i.e., the balance between constructive and destructive phases of the biochemical cycle—is important also for establishing the redox potential of a water. Since most redox reactions are accompanied by proton transfer, a well poised redox potential helps maintain a buffered pH, and, conversely, high buffer capacity tends to maintain the constancy of the redox potential of water.

These considerations are in accord with the recognized principles of ecology; that organisms and their environment are mutually dependent. Not only does the environment determine conditions under which life exists, but the organisms similarly influence the conditions prevailing in their environment (*4*).

Buffer Capacity with Respect to $H_2CO_3^*$. Aeration, photosynthesis, respiration, and many other such phenomena tend to disturb the pH of a water through their respective actions of decreasing and increasing the concentration of dissolved CO_2. Thus the manner in which the pH of a water responds to changes in dissolved CO_2 (more accurately $H_2CO_3^*$) is an important consideration. Since $H_2CO_3^*$ is a weak acid, it is to be expected that the buffer capacity with respect to CO_2 is different from that with respect to a strong acid.

The principles applied to the construction of Figures 1, 2, and 3 and to the evaluation of Equations *C* and *D* in Table I can be employed also in the determination of buffer capacity with respect to any weak acid or weak base. The case for the addition or removal of dissolved CO_2 will be developed in some detail since this case is of particular interest because of the effect of carbon metabolism upon pH. The generalized reaction for carbon metabolism can be given schematically as

$$CO_2 + 2H_2O \underset{\text{Respiration}}{\overset{\text{Photosynthesis}}{\rightleftharpoons}} (CH_2O)_n + O_2 + H_2O \qquad (5)$$

Any addition, $d\,C_{H_2CO_3^*}$, of $H_2CO_3^*$ to a carbonate solution increases both the acidity of the solution and C_T. The alkalinity, however, unlike the case for the addition of strong acid, remains unchanged:

$$\frac{dC_{H_2CO_3^*}}{d\,\text{pH}} = \frac{dC_T}{d\,\text{pH}} = \frac{1}{2}\frac{d[\text{Acidity}]}{d\,\text{pH}} \qquad (6)$$

$$[\text{Alk.}]=\text{const.}$$

Equations developed for acidity and for the buffer capacity with respect to $H_2CO_3^*$ are given in Table I, and representative examples of titration and buffer-capacity curves based on these equations are shown in Figures 4 and 5 for a carbonate system in which alkalinity is constant at 1 meq. per liter. Comparison of Figures 1, 2, 3, and 4 and 5 demonstates that the addition of CO_2 produces a considerably smaller shift in pH than does the addition of an equivalent quantity of strong acid. Equation *F* (Table I) and its graphical representation (Figure 4) are convenient tools for evaluation of biochemical respiration and CO_2 assimilation, and for assessment of metabolic activity from diurnal variations in pH.

Carbonate and Silicate Mineral Deposits. Many of the heterogeneous components of natural water systems such as mineral deposits, clays, and carbonate and igneous rocks contribute significantly to the buffering of these systems with respect to pH. To illustrate the buffering effect of these heterogeneous components let us consider the discharge of a large quantity of acid into a natural water system in which calcium carbonate is a solid-phase component; this would result incipiently in a large decrease in pH. Ultimately, however, the pH decrease, brought about by the addition of the acid, would lead to a dissolution of calcium carbonate until a new calcium carbonate solubility equilibrium obtained. Thus the final change in the pH of the system would be much smaller than the incipient change. Similarly, the addition of strong base would ultimately result in a deposition of calcium carbonate, thus minimizing the pH shift that would occur in the absence of dissolved calcium.

In order to demonstrate quantitatively the pronounced buffering effect of carbonate rocks, an acid-base titration curve for a saturated solution of calcium carbonate ($K_s = 4.7 \times 10^{-9}$) in contact with solid calcium carbonate has been calculated and is represented by Equation *H* in Table I and by Figures 6 and 7. For this example, it has been assumed that $[Ca^{-2}]$ is equal to C_T. Figures 6 and 7 show that approximately 30 m-moles of strong acid are needed

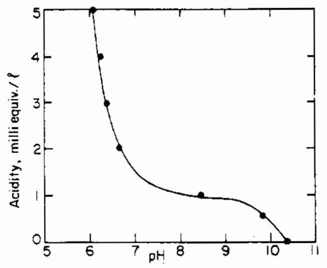

Figure 4. Titration of a carbonate system of 10^{-3} equivalents of alkalinity per liter with CO_2

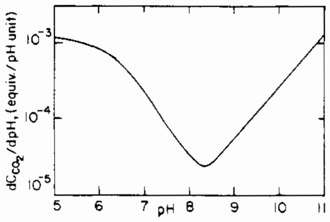

Figure 5. Buffer capacity of a carbonate system of 10^{-3} equivalents of alkalinity per liter with respect to CO_2

Table I. Equations for Acid-Base Titrations and Buffer Capacities in Carbonate Systems

Notation:

(1) [Alkalinity] and [Acidity] defined respectively by Equations 2 and 3 in text;

(2) $[H_2CO_3^*]$ is the sum of $[CO_2]$ and $[H_2CO_3]$;

(3) $K_1 = [HCO_3^-][H^+]/[H_2CO_3^*]$, $K_2 = [CO_3^{-2}][H^+]/[HCO_3^-]$, $K_s = [Ca^{+2}][CO_3^{-2}]$;

(4) $\alpha_1 = 1/(1 + [H^+]/K_1 + K_2/[H^+])$, $\alpha_2 = 1/(1 + [H^+]/K_2 + [H^+]^2/K_1K_2)$.

I. Addition of Strong Base or Strong Acid to Homogeneous Carbonate Solutions

Titration Curves:

$$[\text{Alkalinity}] = C_T\alpha_1(1 + 2K_2/[H^+]) + [OH^-] - [H^+] \qquad \text{(A)}$$

$$[\text{Acidity}] = C_T\alpha_1(1 + 2[H^+]/K_1) + [H^+] - [OH^-] \qquad \text{(B)}$$

Buffer Capacity:

$$\beta = \frac{d[\text{Alkalinity}]}{dpH} = \frac{-d[\text{Acidity}]}{dpH} = 2.3\left[C_T\frac{\alpha_1^2}{K_1}([H^+] + K_1K_2/[H^+] + 4K_2) + [H^+] + [OH^-]\right] \qquad \text{(C)}$$

$$\beta = 2.3\left[\frac{\alpha_1([\text{Alk.}] - [OH^-] + [H^+])([H^+] + K_1K_2/[H^+] + 4K_2)}{K_1(1 + 2K_2/[H^+])} + [H^+] + [OH^-]\right] \qquad \text{(D)}$$

II. Addition (or Removal) of $H_2CO_3^*$ to (from) Homogeneous Carbonate Solutions

$$\frac{d[\text{Alk.}]}{dpH} = 0$$

Titration Curves:

$$C_T = \frac{[\text{Alk.}] - [OH^-] + [H^+]}{\alpha_2(1 + 2K_2/[H^+])} \qquad \text{(E)}$$

$$[\text{Acidity}] = \frac{([\text{Alk.}] - [OH^-] + [H^+])(1 + 2[H^+]/K_1)}{(1 + 2K_2/[H^+])} + [H^+] - [OH^-] \qquad \text{(F)}$$

Buffer Capacity:

$$\beta_{CO_2} = \frac{dC_T}{dpH} = \frac{d[\text{Acidity}]}{2\,dpH} = -1.15\left[\frac{\alpha_1([\text{Alk.}] - [OH^-] + [H^+])([H^+] + K_1K_2/[H^+] + 4K_2)}{K_1(1 + 2K_2/[H^+])} + [H^+] + [OH^-]\right] \qquad \text{(G)}$$

III. Addition of Strong Acid (or Base) to Solutions in Contact with Solid $CaCO_3$

Assumption: $[Ca^{+2}] = C_T$

Titration Curve:

$$[\text{Acidity}] = \left[\left(\frac{K_s}{\alpha_2}\right)^{0.5}(2-\alpha_1 - 2\alpha_2)\right] + [H^+] - [OH^-] \qquad \text{(H)}$$

Buffer Capacity: (see Figure 7)

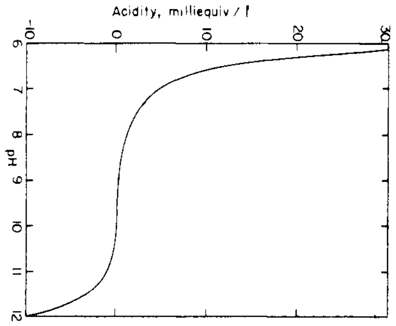

Figure 6. Titration with strong acid of a carbonate system in equilibrium with solid calcium carbonate

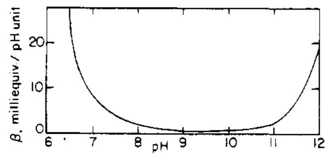

Figure 7. Buffer capacity of a carbonate system in equilibrium with solid calcium carbonate with respect to strong acid

to produce a shift in pH from 8 to 6, whereas for the same solution in the absence of the solid calcium carbonate the same pH shift would require only about 0.5 m-moles of strong acid.

Ion exchange equilibria between dissolved components and sediments and clays, and the decomposition and solution of igneous rocks must also be considered as being among the most significant factors in pH regulation. Sillén (*6*) has suggested that heterogeneous silicate equilibria comprise the principle buffer system in the waters of the oceans. Sillén gives the following reaction as a schematic example of the equilibria involved:

$$3Al_2Si_2O_5(OH)_4\,(s) + 4SiO_2\,(s) + 2K^+ + 2Ca^{+2} + 9H_2O = 2KCaAl_3Si_5O_{16}\,(H_2O)_6\,(s) + 6H^+ \quad (7)$$

Such equilibria are strongly pH-dependent. Although the equilibrium relationships of these reactions are not yet very well understood, it appears reasonable that such exchange reactions exert considerable influence upon the regulation of the hydrogen ion concentration of fresh waters as well as of ocean waters.

Metal-Ion Buffers. Natural waters are buffered not only with respect to hydrogen ion concentration but also with respect to other dissolved constituents. Solubility and exchange equilibria, complex-formation equilibria, and biological activities of the environment all represent metal-ion buffer systems.

Hydrogen ion concentration, carbonate equilibria, and buffer capacity are all related to the solubility equilibria of typical mineral components such as Mg^{+2}, Ca^{+2}, Fe^{+2}, Mn^{+2}, Cu^{+2}, Fe^{+3}, and Al^{+3} (*2*). As an illustration, consider once more the water in equilibrium with solid calcium carbonate. This water will tend to maintain a rather constant pCa even though calcium ions may be introduced to the system from some external source. The buffer capacity concept presented can thus be extended to the prediction of the stability of the water with respect to calcium by quantitative evaluation of expressions such as $dC_{Ca}{++}/d\text{pCa}$. Elucidation of stability with respect to other dissolved cations and anions can be carried out similarly.

Experimental Corroboration. The precision of analytical treatments based on the equations set forth in Table I can be no better than that of the equilibrium constants employed at appropriate temperatures and of the activity corrections applied to account for the nonideal nature of the solutions.

Salinity corrections preferably are applied to the equilibrium constants—by multiplying each of the respective thermodynamic constants by the quotient of the appropriate activity coefficients—rather than to the individual equilibrium concentrations of solute species. The former approach is operationally more meaningful, and permits the establishment of mathematically exact expressions for electroneutrality, alkalinity, and acidity. Larson and Buswell (*3*) have reviewed and summarized data on the acidity constants of $H_2CO_3^*$ and HCO_3^- and the solubility product of $CaCO_3$, valid at different temperatures, and on salinity corrections appropriate for fresh-water systems.

To demonstrate that predictions based on the analytical formulations in Table I are in accord with observed behavior, experimentally obtained points have been plotted along the calculated curves in Figures 2 and 4. The experimental data are in good agreement with the corresponding calculated values.

CONCLUSIONS

The dissolved carbonate system is a mediator and quite reliable indicator of the total buffer system of fresh waters rather than the sole, or even principal, buffering agent. The quantitative interpretation of the nature and interplay of the capacity factors of this indicator is of great practical significance in water technology and limnological sciences.

NOMENCLATURE

C_A = concentration of strong acid
C_B = concentration of strong base
C_T = concentration of total carbonate
f = fraction of strong base
K_1, K_2 = acidity constants of $H_2CO_3^*$
K_S = solubility product of $CaCO_3$
K_w = ion product of water
M = molar
s = solid
β = buffer capacity

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