vestigated. However, a NaCl concentration cell of the type proposed probably is a good one to consider as a power source because (i) it is the usual cell that is constructed in the laboratory and (ii) commercial reversible chloride electrodes have been developed for chlorine production.

It is difficult to compare the osmotic pump or the electrochemical concentration cell as preferred methods of extracting the energy released from the mixing of freshwater and saltwater. One can compare the maximum work that is possible in the two processes. Norman has calculated (*1*) the work W that can be derived from a saline water osmotic pump:

$$W = \frac{RTC}{V} \qquad (11)$$

where C is the concentration of the seawater and V is the volume of water. If one considers the energy to be derived from the addition of 1 liter of freshwater to an infinite amount of seawater, then from (*1*)

$$W = \frac{2 \times 300 \times 1}{1} = 600 \text{ cal}$$

For an electrochemical cell, the free energy or $W_{\max}$ that can be obtained is

$$W_{\max} = n\,F\,\epsilon \qquad (12)$$

where n is the number of equivalents reacting. For a NaCl concentration cell, n equals 1 equivalent per mole of Cl^-. Calculating the energy released when the ions in 1 liter of seawater are transferred to freshwater, one obtains for the electrochemical concentration cell that has been maximized for power generation

$$W = 0.5 \times 23{,}000 \times 0.035 = 400 \text{ cal} \qquad (13)$$

This available work is of the same order of magnitude as that obtained by the osmotic pump, and the generation of electricity by direct means rather than by means of a three-step process has some advantage. The agreement between the calculated $W_{\max}$ in the two processes is not surprising, since these are two ways of deriving energy from the same energy source.

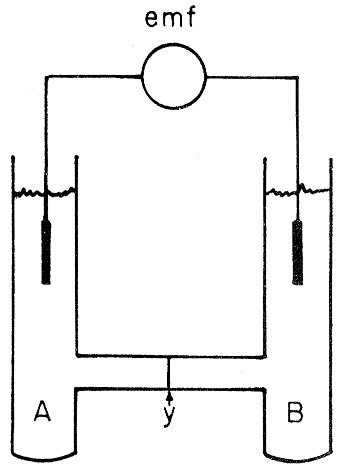

Fig. 1. Electrochemical concentration cell.

There are, however, conceptual differences between the two approaches: in the osmotic pump, water molecules are transported across a membrane; in the electrochemical concentration cell, ions are transported across a membrane. In an interesting practical approach to the use of saline water electrochemical concentration cells as power sources (*6*), ion-exchange membranes have been used to separate the anode and cathode compartments; by this means, one of the most difficult practical problems associated with electrochemical concentration cells has been solved.

Perhaps the biggest obstacle to the use of saline water as an energy source is that the energy-rich phase (that is, the seawater) is in plenteous supply; whereas the energy-poor phase (that is, the freshwater) is in limited supply. Therefore, saline water power plants employing electrochemical concentration cells would need to be located near where rivers enter into the sea or perhaps even in Arctic waters where freshwater could be obtained from the ice.

Another approach would be to use highly saline lakes (for example, the Dead Sea) as the energy-rich phase and seawater as the energy-poor phase. This approach would lead to higher power outputs per electrochemical concentration cell if suitable geographic locations can be found for such installations. It might be feasible to create artificial lakes near the ocean and use solar evaporation to increase their salinity so that energy dissipation can be achieved from the dilution of the saline lake water with seawater.

The sea is being seriously considered as an energy source (*7*). Most of the interest appears to be centered on the use of the thermal gradients in the ocean to generate electric power. On the basis of the evidence presented here, we believe that saline water electrochemical concentration cells and osmotic pumps should be seriously considered as potential long-range power sources.

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Extended Helical Conformation Newly Observed in Protein Folding

Abstract. *A new secondary structure, which shows regularity within the experimental error, is noticed in* α*-chymotrypsin, and considering its extended nature, the name* ϵ*-helix has been suggested for the same. The average observed values of* ϕ *and* ψ *for this conformation are* $-93°$ *and* $+146°$*, respectively. The helical parameters turn out to be* $n = -2.7$ *and* $h = 3.3$ *angstroms.*

During the course of an analysis of the crystallographic structural data of some proteins, which was performed by methods reported recently (*1*), we observed what appears to be a new regular form of secondary structure that apparently has not yet been described. We now report evidence for, and the nature of, this form of chain folding.

The observed overall frequency distribution of θ, which is the torsion angle involving the virtual bonds, namely, $C^{\alpha}_{(i-1)}$—$C^{\alpha}_{(i)}$—$C^{\alpha}_{(i+1)}$—$C^{\alpha}_{(i+2)}$, in six proteins (myoglobin, lysozyme, α-chymotrypsin, carboxypeptidase A, ribonuclease S, and insulin) containing, in all, about 1050 residues is shown in Fig. 1. It may be seen that there is a prominent maximum at $\theta \simeq 50°$, which corresponds to α helices. Apart from this there are two broad maxima, one at $\theta \simeq -135°$ and another at $\theta \simeq -170°$ (*2*).

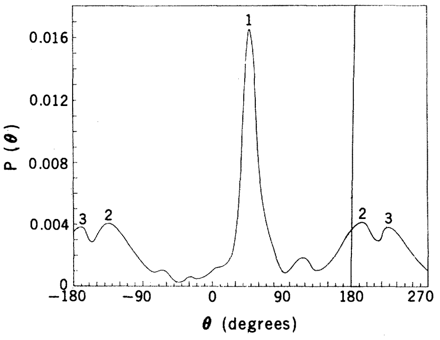


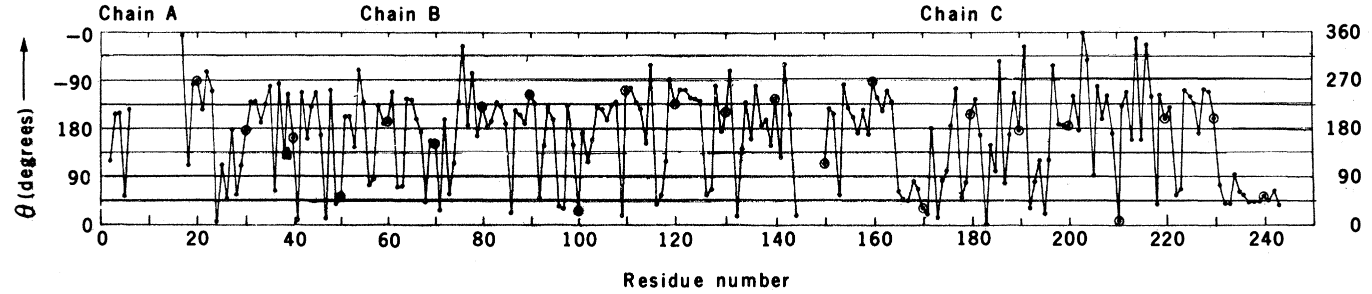
Fig. 1. Overall frequency distribution of θ in six proteins (see text).

Table 1. Values of θ for two stretches in α-chymotrypsin showing approximately constant value. The ϕ, ψ values are also given.

Residue No.	θ (°)	ϕ (°)	ψ (°)
110	−115.6	−121.3	152.2
111	−112.9	− 71.1	159.7
112	−123.4	− 89.2	145.3
113	−123.4	− 93.0	127.2
120	−130.5	−108.5	147.9
121	−117.1	− 78.9	141.5
122	−122.7	− 79.2	157.7
123	−144.1	−101.1	138.4
124	−124.6	− 72.0	+196.9
125	−116.5	−133.7	156.2

Table 2. Coordinates of atoms in a pair of peptide units with $\phi = -93°$ and $\psi = 146°$ corresponding to the conformation for ϵ-helix. The dimensions of the peptide units have been taken from (*5*).

Atom	x	y	z
C_1^α	0.0000	0.0000	0.0000
C_1	0.0000	1.5300	0.0000
O_1	1.0628	2.1686	0.0000
N_2	−1.2058	2.0668	0.0000
H_2	−2.0445	1.5222	0.0000
C_2^α	−1.4358	3.5187	0.0000
C_2	−1.5916	4.0213	1.4366
O_2	−2.1288	3.3175	2.3047
N_3	−1.1107	5.2343	1.6362
H_3	−0.6827	5.7763	0.9130
C_3^α	−1.1564	5.9089	2.9415



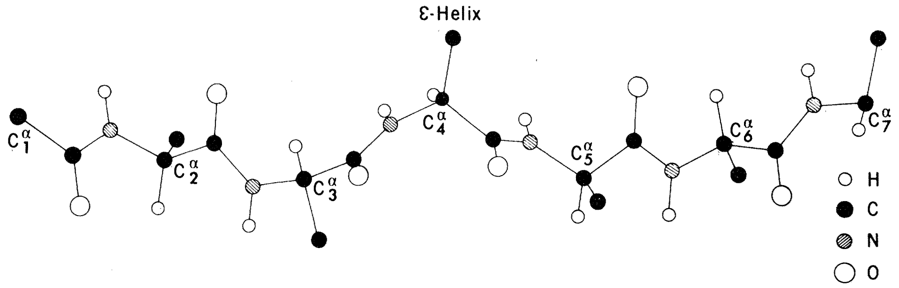


Fig. 2 (above). The θ chain plot for α-chymotrypsin. Fig. 3 (right). A projection of ϵ-helix as viewed normal to its axis.

While the maximum at −170° could be broadly identified with β structures, the one at −135° prompted us to search for possible regular conformation in this region. Since regular conformations exhibit constancy (*3*) of θ value, a search of the θ_i-chain plots of individual proteins was made, to look for stretches with consecutive values of θ_i approximately constant near the region of −135°. In trying to accept such regions the following working rules were applied: (i) there should be at least four successive points on the θ_i plot with approximately constant value and (ii) the deviations in θ should be within ± 20°.

Among the six proteins that were studied, we found that there are two stretches in α-chymotrypsin that satisfy these requirements. They are residues 110 to 113 and 120 to 125 (see Fig. 2). The constancy of (ϕ, ψ) values was next checked (Table 1). The (ϕ, ψ) values are reasonably constant; the probable error quoted by Birktoft and Blow is ~ 15° in ϕ, ψ (*4*). It looks therefore reasonable to characterize these segments as regular and helical (within experimental error). A check on the detailed structure (*4*) indicated that this part is not apparently involved in regular hydrogen bonding. The possibility of these being described as β structures is thus ruled out. The (ϕ, ψ) values fall roughly in region III of the (ϕ, ψ) energy map (*5*). In view of the above findings, it would seem reasonable to describe this conformation as ϵ-helix (ϵ represents the extended nature of the helix). The average values for ϕ and ψ for two stretches (*6*) are found to be −93° and +146°, respectively.

The atomic coordinates for this helix have been generated, taking these mean (ϕ, ψ) values, and are given in Table 2. The n and h values corresponding to these (ϕ, ψ) values are calculated (*5*) to be $n = -2.7$ and $h = 3.3$ Å, and the radius for the helix for the C^α atom is 1.1 Å. A projection of the helix as viewed normal to the helix axis is shown in Fig. 3. It would be of interest to see whether this conformation occurs in other proteins as well.

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2. While a confirmation by inclusion of more data is needed as to whether these are really two maxima or only a single broad maximum, the subsequent discussions in the text are in no way affected.
3. While constancy of θ values for successive segments is a necessary criterion for regular conformation, it is not a sufficient one, since constancy of (ϕ, ψ) values needs to be checked. Nevertheless, plotting the θ_i values helps in selecting the possible region of regular conformation.
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6. In obtaining the mean values of (ϕ, ψ) residues 124 and 125 indicated in Table 1 were excluded since the deviation from the mean is rather large in ψ value for 124 and in ϕ value for 126. The others show relatively less deviation from their means (within ~ 20°).
7. Contribution No. 430, from Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Madras 600025, India.

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Acid Precipitation in the Northeastern United States: *p*H and Acidity

Abstract. *Detailed chemical analyses reveal that acid precipitation* (p*H* < 5.6) *in the northeastern United States is caused by the strong mineral acids sulfuric and nitric. There is a large array of other proton sources in precipitation, weak acids and Brønsted acids; however, although these other acids contribute to the total acidity of precipitation, they have a minimal influence on the free acidity (ambient* p*H) of acid precipitation.*

Precipitation in northeastern United States has a mean *p*H of about 4 (*1, 2*). Atmospheric CO_2 in equilibrium with precipitation would not be expected to produce a *p*H less than 5.6. Thus it has been hypothesized that SO_2 and NO_x (NO and NO_2) from the combustion of fossil fuels are precursors of strong acids in precipitation (*1–4*). This phenomenon of high acidity is not unique to the United States; large areas of Scandinavia downwind of dense industrial complexes receive precipitation with a *p*H of 4 or lower (*3, 4*).

Elucidation of the acid precipitation (*p*H < 5.6) phenomenon depends upon the answer to the following question: What chemical compounds found in precipitation cause acidity, and to what degree? This question is best answered by complete chemical analysis of the precipitation. Analysis of over 1500 precipitation samples in northern New Hampshire showed that the ambient *p*H of precipitation was caused by the strong acids H_2SO_4 and HNO_3 (*1, 2*). This finding was also the conclusion of workers in Scandinavia (*4*). Frohliger and Kane (*5*), however, concluded that acid precipitation was caused by unidentified weak acids. This conclusion was based solely on the determination of *p*H and total acidity in 26 precipitation samples collected during one winter in Pittsburgh, Pennsylvania. The specific deficiencies in their approach have been dealt with elsewhere (*6*). We present here results of an investigation on the relative effect of strong acids (for example, H_2SO_4 and HNO_3), weak acids (for example, organic acids and H_2CO_3), Brønsted acids (for example, dissolved Al, dissolved Fe, and NH_4^+), and particulate matter on the free and total acidity of precipitation as determined by titration, chemical analysis, and equilibrium calculations.

Precipitation samples (rain or snow only, no dry deposition) were collected in thoroughly rinsed, acid-washed containers, plastic for inorganic analysis and glass for organic analysis. Samples were stored at 4°C until analyzed, usually less than 1 week for the inorganic constituents. Organic acids were analyzed immediately after individual storms. There was no significant change in the inorganic composition of these precipitation samples when stored at 4°C if the *p*H of the sample was < 5 (*7*).

Analyses for Ca^{2+}, Mg^{2+}, K^+, Na^+, Al^{3+}, Fe^{3+}, and Mn^{2+} were carried out on an atomic absorption spectrophotometer (Perkin-Elmer model 403) equipped with a graphite furnace (Perkin-Elmer HGA 2100). Standard procedures adapted for use with a Technicon Autoanalyzer were used for the analysis of NH_4^+, NO_3^-, SO_4^{2-}, PO_4^{3-}, Cl^-, and H_4SiO_4 (*7*). We determined organic acids (C_1 to C_{10} volatile carboxylic acids) by using column and gas chromatography (*8*) and mass spectrometry (*9*). Ambient *p*H determination and titrations to *p*H 9.0 were carried out with a *p*H meter (Sargent-Welch PBL), equipped with a combination electrode. The measurement of *p*H with this system was accurate to ± 0.03 *p*H unit, which introduces a 6 to 7 percent error in the calculation of the [H^+]. Therefore, at *p*H 4.00 [H^+] would be 100 ± 7 μeq/liter.

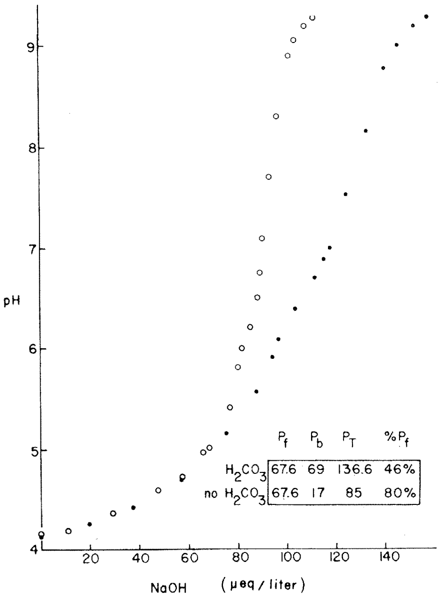

Fig. 1. The effect of H_2CO_3 on the free, bound, and total acidity of precipitation. The open circles represent an aliquot from a sample from which the H_2CO_3 has been removed by N_2 purging. The closed circles represent an aliquot of the same sample with the H_2CO_3 present. The symbols P_f, P_b, and P_T represent, respectively, the concentration of free protons, bound protons, and total protons (in microequivalents per liter); P_b is determined by difference, $P_T - P_f$. The symbol $\%P_f$ represents the percentage of the total protons that are free.

For all precipitation samples that we have collected in the rural northeastern United States the *p*H has been < 5. Since H_2CO_3 does not contribute to the free acidity below *p*H 5 (*10*), we excluded this acid by flushing the samples with N_2 so as not to mask other possible contributors (*11*). The actual effect of H_2CO_3 on the free and total acidity is demonstrated by the following experiment (Fig. 1). Two aliquots of the sample were titrated identically. In one (open circles in Fig. 1), all of the H_2CO_3 was removed by the bubbling of N_2 through the sample prior to titration. During the titration of this sample, a N_2 atmosphere was maintained over the surface. Thus the influence of H_2CO_3 was eliminated, and the effect on the free acidity could be determined. In the second (closed circles in Fig. 1), no N_2 was used; that is, the titration was done under a normal laboratory atmosphere.

Two conclusions can be drawn from this experiment. (i) Carbonic acid has no influence on the measured *p*H of this precipitation sample and indeed has no effect on the measured *p*H of any aqueous sample with a *p*H < 5 that is in equilibrium with the atmosphere (*10*). (ii) Although it has no effect on the free acidity, H_2CO_3 has a potentially large effect on the total acidity when titrated to *p*H > 5 because of the increasing solubility of CO_2 as the *p*H increases. The solubility of CO_2 at *p*H < 5 is 20 μeq/liter and at *p*H 9 is 5000 μeq/liter (*10*). If H_2CO_3 were removed, such titrations would reflect exchange rates of CO_2 between the atmosphere and the water sample as influenced by stirring and other operations, and would be totally misleading with respect to the proton chemistry of the initial sample.

In an aqueous medium, such as precipitation, protons may exist in two states, free and bound, and together they constitute the total acidity. Free protons consti-