acid substitutions, Gautier (*10*) infers by various assumptions only 150. Of these 150, 63 are disqualified as elements of a valid transition matrix because they are multiple-step substitutions. Of the remaining 87, 34 are each based on a single *inferred* mutation. One such case is Arg → Lys. From sampling error, the true number of substitutions could well be two or three rather than one. The reverse mutation Lys → Arg occurs only eight inferred times with an associated error of about ± 3. This could explain entirely Gautier's abnormal result where the transition probabilities for Lys → Arg and Arg → Lys are listed as .0108 and .0048 (*10*), whereas Dayhoff finds (*3*) probabilities of .0023 and .0065, which are different both in magnitude and direction from the values calculated by Gautier. His finding that there are "more replacements of lysine to arginine than the converse" is therefore insupportable. Lysine is consistently present in most proteins at levels higher than those expected from the genetic code, while the reverse is true for arginine (Table 1). There is no observed phylogenetically dependent increase in arginine with respect to lysine in contemporary proteins. For a given protein family the proportions of these two amino acids is remarkably stable: for the cytochromes c isolated from 64 species, the percentage of lysine is 14.3 ± 2.5 (standard deviation) percent and of arginine 2.2 ± 0.6 percent. Gautier himself concludes (*10*) "Cependant le nombre trop faible de mutations décelées ne nous a pas permis d'obtenir des résultats certains sur ce problème des tendances." Gautier's discussion has no bearing on the "evolutionary intruder hypothesis," which refers to an event postulated to have occurred 2 billion or 3 billion years ago, before the present genetic code was in existence.

Glycine can be a helix-breaker, is less hydrophobic than alanine, and would be expected to be selected against relative to alanine in the interior of a molecule. Alanine is not a helix-breaker, is more hydrophobic, and is small enough to act as a "filler."

Our model for the interaction between "selective and neutral mutations to give a picture of dynamic equilibrium in protein evolution" can be obscure only if one has not read the literature (*11*). Gautier's supposition of what we mean is wrong: We do *not* believe and have not stated that the amino acids in the "expected range pool" replace each other without any action of natural selection. We did not state that all or most isoleucine and valine interchanges are neutral; some may be, and, for those, genetic drift would play a part.

Table 1. Amino acid distribution per 61 residues. The codons for Arg, Cys, Gln, Glu, Gly, Leu, Lys, Ser, Trp, and Tyr can each go to a chain-terminating codon by a single base change. The frequency of occurrence of Gln, Glu, Gly, Lys, and Tyr is incompatible with any hypothesis which states that "amino acids which possess codons that can go to a chain-terminating codon in one step are selected against."

Residue	a*	b†	c‡	d§	e‖
Ala	4	5.3	5.2	5.3	4.9
Arg	6	2.6	2.7	2.8	2.4
Asn	2	3.0			2.7
Asp	2	3.6			2.9
Asx	(4)	(6.6)	(6.5)	(6.3)	0.5
Cys	2	1.3	1.4	0.7	2.1
Gln	2	2.4			2.2
Glu	2	3.3			2.9
Glx	(4)	(5.7)	(6.5)	(6.6)	0.6
Gly	4	4.8	4.9	4.7	4.6
His	2	1.4	1.3	1.2	1.3
Ile	3	3.1	3.0	2.6	2.8
Leu	6	4.7	3.9	5.1	4.5
Lys	2	4.1	3.9	4.1	4.3
Met	1	1.1	1.1	0.9	1.0
Phe	2	2.3	2.3	2.4	2.1
Pro	4	2.5	2.9	3.0	3.4
Ser	6	4.5	3.8	4.7	4.8
Thr	4	3.7	3.5	3.6	4.0
Trp	1	0.8	0.8	0.5	0.7
Tyr	2	2.3	2.0	2.2	2.1
Val	4	4.2	4.1	4.2	4.2

*From the genetic code table. †From (*4*). ‡From (*1*). §From (*2*). ‖From (*3*).

Because of the paucity of data or references to the literature in Gautier's comment, and the variance of his theoretical inferences from a significant body of experimentally established fact, we cannot credit his conclusions.

We observed in preparing Table 1 (footnote) that five of the ten amino acids which possess codons that can mutate to a chain-terminating codon by a single nucleotide replacement are present in frequencies in excess of expectation (Table 1). One might have anticipated a selection against these ten amino acids, but, as a class, such codons are clearly not strongly selected against.

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5. Abbreviations for the amino acid residues are as follows: Ala, alanine; Arg, arginine; Asp, aspartic acid; Asn, asparagine; Cys, cysteine; Gln, glutamine; Glu, glutamic acid; Gly, glycine; His, histidine; Ile, iosleucine; Leu, leucine; Lys, lysine; Met, methionine; Phe, phenylalanine; Pro, proline; Ser, serine; Thr, threonine; Trp, tryptophan; Tyr, tyrosine; and Val, valine.
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27 September 1976

Acid Precipitation: Strong and Weak Acids

In a recent report Frohliger and Kane (*1*) have made various assertions concerning the acid character of rain. Their concluding remarks (*1*) perhaps best summarize these assertions: "The presence of weak acid species in precipitation casts additional doubt on the idea that the *p*H of rainfall was ever controlled by the solubility of CO_2 in the precipitation and discredits the assumption that strong acids account for the presently observed *p*H value." Considering the scientific and environmental implications of this statement, a careful and complete examination of the facts and their interpretation is in order.

Frohliger and Kane report on samples from 26 selected precipitation events collected during a 5-month period (December through May) in Pittsburgh, Pennsylvania (*2*). The data are in the form of two chemical parameters per sample, *p*H and total acidity (integrated over a *p*H range of < 5 to $\simeq 9$). They report *p*H values ranging from 4.12 to 5.78, and a buffer intensity 2 to 100 times greater than anticipated for pure water or an unbuffered acid, and then infer that the proton donors in their precipitation samples are weak acids. From these data, they discount the presence and function of strong acids in precipitation. They arrive at the latter conclusion by means of an incomplete syllogism. Their arguments run as follows: if weak acids are present in precipitation, then strong acids are not present in precipitation. The coexistence of weak and strong acids in solution and their relative roles *in controlling pH* are not considered.

The specific issue, however, is exactly what acid species were responsible for the ambient *p*H values that Frohliger and Kane observed. Total acidity values as reported by Frohliger and Kane are informative but not adequate to answer this question. Only a complete chemical analysis of their samples would provide the necessary information. Lacking such independent data, total acidity values can be variously interpreted.

The presence of weak acid, notably carbonic acid, is well documented in contemporary precipitation (*3*) and in fossil precipitation preserved as glacial ice (*4*). From a historical perspective, the *p*H of glacial ice (10^2 to 10^4 years old) is particularly interesting; *p*H values are generally greater than 5 (*4*) and thus are consistent with the prevailing concept of "normal rain" (*5*). The presence of weak acids in precipitation is not seriously questioned by others who have addressed the problem of "acid rain." On the contrary, those of us engaged in the Hubbard Brook Ecosystem Study have already made a point of the role and functioning of weak acids in precipitation (*6*).

Weak organic acids with low *pK* values (where *pK* is the negative logarithm of the equilibrium constant) could contribute to the free and total acidity of precipitation if present in substantial quantities (that is, $\gtrsim 1$ mg/liter). However, Frohliger and Kane have not chemically identified any such acids in their samples. We have found that in other areas of the northeastern United States organic acids are present only irregularly and in very small amounts in precipitation (*6*). Weak organic acids with high *pK* values such as phenols and polyphenols would be included in any integrated acid analysis if the titration were continued to values as high as *p*H 9. Yet such acid species would be almost completely undissociated at $pH < 5$ and would, consequently, exert no sensible control on *p*H values at the low end of the *p*H scale. The average annual *p*H of precipitation over the northeastern United States currently is less than 5 (*7, 8*).

By titrating over a large *p*H range (< 5 to $\simeq 9$), Frohliger and Kane have included a spectrum of potential proton donors in addition to weak acids per se. Proton donors of this sort are called Brønsted acids (*9*, p. 70). Likely Brønsted acids in precipitation include NH_4^+, dissolved Al, dissolved Fe, silica particles, clay particles, and organic detritus. Any of these substances present in sufficient amounts could completely account for the observed total acidity in the precipitation samples collected by Frohliger and Kane. For example, 0.5 mg of NH_4^+ per liter and 0.5 mg of Al^{3+} per liter could provide 28 and 56 μeq/liter, respectively, in a total acidity titration done from *p*H 4 to 9. Before the total acidity values of Frohliger and Kane can be uniquely attributed to weak acids, it is necessary to show that Brønsted acidity is no factor in their samples (*10*).

Table 1. Arithmetic mean of the annual bulk precipitation at the Hubbard Brook Experimental Forest in New Hampshire during 1963–1974. Results are based on chemical analyses of samples obtained weekly throughout each year. The cation and anion sums are not statistically different.

Ion	Mean concentration (μeq/liter)	Standard deviation of the mean (μeq/liter)
Ca^{2+}	8.6	1.1
Mg^{2+}	3.7	0.7
K^+	1.9	0.5
Na^+	5.4	0.6
NH_4^+	12.1	0.7
H^+	73.3	3.0
SO_4^{2-}	59.7	2.4
NO_3^-	23.1	1.7
Cl^-	14.4	2.5
PO_4^{3-}	0.25	

Sum for cations = 105.0 ± 3.4 μeq/liter
Sum for anions = 97.45 ± 3.9 μeq/liter

Carbonic acid represents a special case. If a water sample were in continuous equilibrium with the atmosphere, H_2CO_3 and its dissociation products would contribute 20 μeq/liter at *p*H 5 and about 5000 μeq/liter at *p*H 9 to the experimentally measured total acidity via titration (*9*, p. 127). In contrast, the free acidity (ambient *p*H) of a precipitation sample at *p*H 5 would be about 10 μeq/liter. At $pH < 5$, H_2CO_3 would be virtually undissociated and thus not contribute at all to the ambient *p*H value (*9*, p. 127). Obviously, great care must be exercised during the titration of a precipitation sample to avoid the inclusion of CO_2 from the atmosphere; otherwise, misleading data on the relationship between the total acidity and free acidity of ambient precipitation samples could be obtained. Since CO_2 apparently was not excluded during titration of the precipitation samples studied by Frohliger and Kane, their results are highly questionable (*1, 11*).

Because Frohliger and Kane have not accounted for the state of CO_2, Brønsted acids, or weak organic acids in their precipitation samples, the meaning of their total acidity values is therefore equivocal, and their conclusions about the source of proton donors in precipitation are unsubstantiated and unwarranted.

In the Hubbard Brook Ecosystem Study over 1500 precipitation samples have been collected and chemically analyzed during the past 11 years (Table 1). Results have included data on total inorganic chemistry, organic acid analysis, and acid-base titrations. The ionic balance in the precipitation chemistry at Hubbard Brook argues that, overall, no major anionic constituents have been missed. These data describe a dilute solution of H_2SO_4 and HNO_3 with some contaminants, and therefore strong acids are responsible for the ambient *p*H in this rural forested area. Any other interpretation of these data would require the postulation of strange or extraordinary chemical effects. Similar long-term chemical data from the eastern United States and northern Europe make a powerful case for the presence of strong acids in contemporary precipitation on both a local and a regional basis (*7, 12*).

The predominance of unbuffered, strong acids in precipitation at Hubbard Brook is further demonstrated (i) since Cogbill and Likens (*8*) have shown that *p*H may be calculated with high precision from a stoichiometric relationship between the major ions in precipitation at $pH < 5$ and (ii) since the slope of titration plots for H^+ concentration versus the concentration of strong base for precipitation samples at $pH < 5$ is -1.

In summary, the meaning of the total acidity data published by Frohliger and Kane is impossible to assess, given the incomplete information on collection and analytical techniques and the absence of complementary chemical data. Furthermore, their data base is severely limited in both time and space. Yet, from these data sweeping generalizations were made about the chemical nature of rainfall around the world and in the geologic past. Because of their ambiguous nature, the data of Frohliger and Kane are not illuminating regarding the acid chemistry of precipitation. Certainly these data do not provide any basis for dismissing the presence of strong mineral acids in precipitation as Frohliger and Kane have done.

The central question in the "acid rain" problem is not whether weak acids are present in precipitation. Rather the serious issues are the following: Do the strong acids and heavy sulfur and nitrogen loads in some contemporary precipitation come from anthropogenic sources? What trends exist in the geographic distribution and intensification of acid precipitation? What are the environmental stresses elicited by both strong and weak acids in precipitation? Scientists addressing these and like problems are entitled to the usual standards of quality control for data published in their fields.

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17 September 1975

Frohliger and Kane (*1*) have drawn some inferences about the nature of the acid present in precipitation as a result of an analysis of 26 precipitation samples. However, on the basis of the experimental details in their report, I have considerable doubt about the accuracy of their results and thereby about the validity of the conclusions based on those results.

First, all of their results are based on the analysis of precipitation samples which had been preserved by freezing. It is therefore crucial to the arguments of Frohliger and Kane that no changes took place in their samples after collection but before analysis, and yet they report no control experiments to demonstrate that no changes in the samples took place. In fact, such changes might be expected to occur because precipitation has little buffering capacity and thus is very susceptible to changes in *p*H. Roberson *et al.* (*2*) have reported on the marked changes in *p*H that can take place in such waters when the measurement of *p*H is delayed, even when the sample is kept in a completely full, sealed container. Philbert (*3*) has reported that the preservation by freezing of the relatively unbuffered waters of Lake Ontario and Lake Huron leads to changes in the alkalinity of such samples.

Both Roberson *et al.* and Philbert give a number of possible explanations for the observed changes. Two of these are the loss of dissolved CO_2 and the precipitation from solution of materials that do not readily redissolve. It is well known that dissolved gases are expelled from liquids upon freezing. Thus it would not be surprising if much of the CO_2 and other gases present in the acidic precipitation samples of this study were lost when the "almost full" sample containers were frozen. This loss of dissolved gases would lead to an increase in *p*H and thus to a decrease in the free acid present in the thawed samples. Also, as freezing occurs, the liquid remaining becomes progressively more concentrated. Thus dissolved materials from rainfall or thawed snow samples undergoing freezing may precipitate out. Other reactions such as the exchange of protons for cations on particulate matter in the freezing solutions could be promoted at the higher concentrations.

To check on the stability of *p*H in frozen precipitation samples, I have taken and remeasured the *p*H of 21 precipitation samples collected in Chicago over the past 2 years for which initial *p*H measurements had been made immediately upon collection. These samples had been collected in polyethylene buckets and had been kept frozen in polyethylene containers since their collection except for one or more thawings to remove representative portions for other analyses. When these samples were thawed and their *p*H was remeasured, it was found to have increased by an average of 0.54 ± 0.68 *p*H unit; that is, the free acid present had decreased by a factor of 3.4. The changes ranged from a decrease of 0.24 *p*H unit to an increase of 2.42 *p*H units. For comparison, the average difference between the free and total acid for each of the samples reported in the study of Frohliger and Kane was calculated from the data in their table 2 to be a factor of 6.47.

Second, although Frohliger and Kane demonstrated that precipitation samples are buffered below *p*H 7, part of their proof rests on the assumption that these same samples are not buffered above *p*H 7. This is done in equation 5 where they assume that the excess base used in the titration, OH^{-}_{xs}, can be calculated just by measuring the *p*H of the solution after the titration is complete. If this final solution is at all buffered above *p*H 7, then this correction for excess base used in the titration will be too low and will result in a value for the total acid in their samples which is high. The few titrations that have been carried out in our laboratory on precipitation samples (*4*) indicate that these samples are buffered above *p*H 7 as well as below. This buffering at high *p*H could be due to such basic materials as NH_3, proteins, and silicates, which are known to be present in precipitation. Moreover, if the solutions being titrated were not protected from the atmosphere, the absorption of CO_2 by the solution would continually increase the magnitude of this error. A further complication is that the final *p*H in the titrations of Frohliger and Kane was different for each sample titrated.

In their control experiments for the titration Frohliger and Kane utilized H_2SO_4. However, because H_2SO_4 is a strong acid, it does not show buffering effects in the range of the *p*H measurements as the precipitation samples do.

Finally, small precipitation events usually have higher concentrations of particulate matter and gases scavenged from the atmosphere than big events. Likewise, the early precipitation in a big event is usually more concentrated in scavenged material than the later precipitation in that event (*5*). In the study conducted by Frohliger and Kane, a maximum of one bottle of precipitation was collected for each event. This type of sample selectivity could bias any results obtained (*6*), making them unrepresentative of the precipitation as a whole.

The major result of the study of Frohliger and Kane is that the total acid concentration of precipitation is much higher than the free acid concentration. However, the two possible sources of error discussed above either decrease the free acid concentration or increase the total acid concentration and thus these errors might be responsible for many of the differences found.

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8 September 1975

Frohliger and Kane (*1*) have reported acid-base titration figures for precipitation samples from a suburban site in Pennsylvania, and they have drawn some conclusions that are not fully substantiated by the data presented. Data from the European Air Chemistry Network (*2*), as well as from measurements in connection with the OECD Programme (*3*), indicate that the main chemical species in precipitation are SO_4^{2-}, NH_4^+, and NO_3^-. The precipitation acidity (free H^+ at $pH \lesssim 5$) is generally determined by the difference

$$[H^+] = 2[SO_4^{2-}] + [NO_3^-] - [NH_4^+]$$

If the titration procedure described by Frohliger and Kane is used, some NH_4^+ ions ($pK_a = 9.25$ at 25°C, where pK_a is the negative logarithm of the dissociation constant) and dissolved CO_2 will be titrated as weak acids. In order to understand the significance of the results of Frohliger and Kane, it is necessary to know the concentrations of NH_4^+ and the precautions taken to remove CO_2 from the precipitation samples.

Table 1. Precipitation chemistry data from Birkenes, Norway, April to June 1973 (48 samples).

Ion	Weighted mean concentration	Weighted standard deviation from the mean
H^+	$68 \times 10^{-6}M$	$39 \times 10^{-6}M$
NH_4^+	$47 \times 10^{-6}M$	$34 \times 10^{-6}M$
NO_3^-	$31 \times 10^{-6}M$	$24 \times 10^{-6}M$
SO_4^{2-}	$44 \times 10^{-6}M$	$28 \times 10^{-6}M$

A program of chemical analysis for precipitation samples should include *specific* methods for determining the concentrations of SO_4^{2-}, NH_4^+, NO_3^-, and other components. It should also be realized that $(NH_4)_2SO_4$ may act as a strong acid in a natural ecosystem. Our experience (*3*) is that the proportion of NH_4^+ to SO_4^{2-} increases in air masses with continental origin. In contrast to Frohliger and Kane's reference to Granat's results (*2*), we find a very high correlation between SO_4^{2-} and free H^+ at Norwegian sites (correlation coefficient $r = .8$ to $.9$). Typical concentrations of major components are shown in Table 1. Obviously, the good correlation is due to the high acidity. Sites with higher NH_4^+ concentrations will give poor correlation.

Weak organic acids are probably also present in precipitation samples. We feel, however, that more direct evidence is required to prove their occurrence in significant amounts. The chemical composition must also be known if the ecological effect is to be considered.

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7 October 1975

I object strongly to the conclusions of Frohliger and Kane (*1*). Their data, with which I have no quarrel, indicate that Pennsylvania rainfall can contain as much as 43×10^{-5} mmole/ml of "weak acids," while the "free $[H^+]$" is usually less than 8×10^{-5} mmole/ml. This finding, they claim, "discredits the assumption that strong acids account for the presently observed pH value." The fact is that weak acids exert no control over the pH of a solution which has a pH much smaller than the pK_a (the negative logarithm of the equilibrium constant) of the acid; that is, once the weak acid is totally in the protonated form (HA), a stronger acid can lower the pH just as it would if no weak acid were present.

It may indeed be that the dissolution of anions of weak acids (A^-) might raise the pH of a mineral acid solution by removing some of the free H^+; this dissolution could account for the lack of the correlation between the free H^+ and anions such as SO_4^{2-} in precipitation. One might, in fact, expect to find a fair amount of such weak acids and their anions in an atmosphere where substantial quantities of coal are burned. Since the pK_a of the most common carboxylic acids is in the range of 4 to 5, it is even possible that there are some unprotonated anions present. Their *degree* of protonation, however, and therefore the pH, can easily be altered by the addition of a stronger acid, such as H_2SO_4. For this reason I must argue that the presence of large quantities of weak acid in rainfall is *not* inconsistent with the idea that the species lowering the pH is H_2SO_4 or some other strong acid.

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2 September 1975

Frohliger and Kane (*1*) have reported data they claim supports the hypothesis that acidic precipitation is a solution of weak acids. There is no evidence for this hypothesis from European precipitation samples, in which the measured pH is in good agreement with the predicted acidity based on the concentrations of major ions (*2*). Furthermore, the experimental data offered by Frohliger and Kane do not provide evidence for the weak acid hypothesis.

The titrations described by Frohliger

Table 1. Chemistry and titration data for precipitation collected in Oslo, Norway. Means and standard deviations of quadruplicate determinations are expressed as micromoles per liter.

Component	Episode 1, 2 October 1975	Episode 2, 4–5 October 1975
Free acid, $[H^+]$	57 ± 4 (pH 4.25)	18 ± 2 (pH 4.75)
$[NH_4^+]$	42 ± 3	6 ± 4
$[H_2CO_3]$	12	12
"Total acid" calculated, [HA], that is, $[H^+]$ + $[NH_4^+]$ + $2[H_2CO_3]$	123 ± 7	48 ± 6
"Total acid" titrated, [HA]	With N_2, 109 ± 8 Without N_2, 135 ± 4	With N_2, 45 ± 15 Without N_2, 80 ± 24
$[SO_4^{2-}]$	47 ± 3	15 ± 4
$[NO_3^-]$	29 ± 2	3 ± 1
"Total acid" due to titration procedure (%)	20	45

and Kane were not carried out in a CO_2-free environment; an appreciable amount of the titrant was used merely to neutralize the atmospheric CO_2 that is incorporated into the sample during the titration. If titrations are carried out in an N_2 environment, much of the "total acid" disappears.

We collected rain near Oslo during two events and titrated quadruplicate samples, using Frohliger and Kane's procedure and also in an N_2 environment. In addition, we measured in triplicate the concentrations of SO_4^{2-} and NO_3^-, the two principal anions in acid rain, and NH_4^+, a common constituent of acid rain. We calculated the dissolved CO_2 concentrations using a partial pressure for CO_2 of 3.2×10^{-4} atm and a solubility of 39 moles of H_2CO_3 per liter of water per atmosphere of CO_2 at 20°C (*2*).

The results (Table 1) demonstrate that the amount of "total acid" depends on the titration procedure. Without taking precautions to exclude atmospheric CO_2 during titration, 20 to 50 percent of the "total acid" is due to the incorporation of atmospheric CO_2. In a CO_2-free environment the titrated "total acid" is due to a combination of the free acid, NH_4^+, and dissolved CO_2 in the fresh sample. The SO_4^{2-}, NO_3^-, and free acid concentrations show that these acid precipitation samples are dilute solutions of strong acids, namely, H_2SO_4 and HNO_3; there is no evidence for a significant contribution from weak acids.

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References and Notes

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2. L. Granat, *Tellus* **24**, 551 (1972).
3. We thank Y. Aartun for technical assistance.

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There appear to be two major concerns over our report (*1*) on the weak acid nature of precipitation. The first centers around the methodology of our titration procedure. The second is related to the interpretation of the results. We would like to describe an experiment which should answer both questions at the same time.

In May 1975, Cowling (*2*) asked us to use our procedure to analyze samples of simulated rain similar to that used in a research project of Shriner (*3*). The results of these analyses together with the analyses of two actual rain samples are shown in Table 1.

Table 1. Comparison of synthetic rain and actual rain; ppm, parts per million; N.D., not detectable; $[HA]_T$, total acid present in solution.

Sample	*p*H	$[H^+]$ (mole/liter)	$[HA]_T$ (mole/liter)	*pK*	$[SO_4^{2-}]$ (mole/liter)	Sulfate (ppm)	$[H^+]/[SO_4^{2-}]$
Synthetic pure	5.61	2.46×10^{-6}	3.75×10^{-5}	6.8	N.D.	N.D.	
Synthetic pure	5.47	3.39×10^{-6}	3.76×10^{-5}	6.5	N.D.	N.D.	
Synthetic acid	3.19	6.46×10^{-4}	5.69×10^{-4}	$\propto$	2.68×10^{-4}	25.8	2.1
Synthetic acid	3.21	6.17×10^{-4}	6.11×10^{-4}	$\propto$	2.81×10^{-4}	27.0	2.2
Actual rain*	4.12	7.59×10^{-5}	1.54×10^{-4}	4.1	2.71×10^{-5}	2.6	2.8
Actual rain†	4.29	5.13×10^{-5}	2.88×10^{-4}	4.9	8.33×10^{-5}	8.0	0.61

*7 to 9 April 1974. †17 May 1974.

The samples labeled "synthetic pure" are Cowling's deionized water. Our analysis shows that this sample is indeed a dilute solution of a weak acid with a *pK* value (the negative logarithm of the equilibrium constant) of about 6.6. The pK_1 of carbonic acid is 6.4.

The samples labeled "synthetic acid" are the same deionized water with H_2SO_4 added to yield a *p*H of 3.2 ± 0.1. The measured *p*H of this solution was 3.2 ± 0.01. The 10 percent accuracy of the titration procedure is due to the fact that the calculation is based on two *p*H measurements. The titration does not show the incorporation of atmospheric CO_2 during the titration. The ratio of $[H^+]$ to $[SO_4^{2-}]$ is also within 10 percent of the stoichiometric ratio. The results are within our acceptable error limits.

The last two samples listed in Table 1 are actual rain samples collected at our collection site. Neither these samples nor the other rain samples examined in this laboratory yield constituent values that could be identified with either the synthetic pure or the synthetic acid samples.

Our acidity study shows that precipitation has some buffering capacity. Precipitation has a reservoir of H^+. At this stage of our research, we are not able to speculate on the composition of precipitation except to point out that it does not have the chemical characteristics of a dilute H_2SO_4 solution or of a mixture of mineral acids. Since precipitation collected at the present time is more than a dilute solution of mineral acids, it is difficult to postulate that at some time in the past the acidity of precipitation was controlled solely by the solubility of CO_2 in water.

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