

infinite dilution. This is certainly reasonable for the aqueous phase, in which the values of the activity coefficients depend on the ionic strength, and in which the ionic strength will barely be affected by changes in the low concentrations of Gd^{3+} . If the same standard state for Gd^{3+} is chosen for all phases, then relative to its value in the aqueous phase, the free ion activity coefficient for Gd^{3+} in the silicate liquids is only about 0.006. On that basis, the assumption which is sometimes made that cations present in trace quantities in a silicate liquid behave as they do in aqueous solution would appear to be a very poor one, at least for the rare earths.

The reaction between a complexing agent (L^{-x}) and Gd^{3+} in a silicate liquid might be represented by the following equation:



From the equilibrium constant for this reaction, it is seen that the free ion activity of Gd^{3+} would be proportional to the total concentration of Gd in the solution and would vary as the reciprocal of the concentration of the complexing agent to the n th power. Since the effect in nature and in our experiments of the composition of the silicate liquids on the distribution coefficients appears to be small, it is inferred that the entity responsible for lowering the free ion activity of Gd^{3+} is present in copious and approximately constant concentrations in common silicate liquids. If so, as long as the assumptions leading to Eq. 1 are valid, knowledge of distribution coefficients for rare earths is of as much practical use as knowledge of the appropriate activity coefficients for predicting equilibrium concentrations.

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6. Starting mixes were prepared from oxides supplied by Spex Industries Metuchen, N.J. Upper limits of <1 ppb Gd in these oxides and <1 ppb Gd in the deionized water were set by neutron activation analysis. Capsules were not buffered with respect to oxygen fugacity because of the stability of the Gd ion in the $+3$ state.
7. No measurements of the solubility of $GdCl_3$ in water above its critical temperature ($647^\circ K$) have been made, but water at the pressure and temperature of these experiments is known to be an excellent solvent for NaCl [S. Sourirajan and G. C. Kennedy, *Univ. Calif. Radiat. Lab. Rep. No. 6175* (1960); *Amer. J. Sci.* **260**, 115 (1962)].

8. These obsidians are from Hawaii and Lipari, Italy, and their respective compositions in percentage (by weight), as obtained by electron microprobe measurements, are: SiO_2 , 77.1, 75.0; Al_2O_3 , 12.1, 12.9; Fe as FeO, 1.08, 1.60; MgO , 0.00, 0.05; CaO , 0.37, 0.71; Na_2O , 3.67, 4.03; K_2O , 5.23, 5.32; TiO_2 , 0.09, 0.09; MnO , 0.02, 0.07; H_2O , 0.45, 0.36 (by difference). Their Gd concentrations are <10 ppm.
9. We thank Drs. P. R. Bender and C. D. Cornell for helpful suggestions. Supported in part through funds administered by the Research Committee of the Graduate School of the University of Wisconsin and by NSF grants GA-1655 and GA-14070.

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Microwave Noise from Rainstorms

Abstract. *Observations of microwave noise due to rainstorms have been made at 1415 Mhz. The observed effect may well be due to electrical discharge between water droplets.*

It has been suggested that electric discharges occur between charged water droplets during rainstorms, and further that these discharges will produce broadband noise extending into the microwave region (1). The intensity of this noise is predicted to be between $20^\circ K$ and $100^\circ K$ equivalent noise temperature. Since such an effect would be easily detectable with standard techniques of radio astronomy, we looked for it during the spring and summer of 1969 (2).

The observations were made at 1415 Mhz with a 20-foot horn-reflector antenna (2° beam width). This frequency is appropriate, because it is sufficiently low that rain attenuation and associated thermal radiation are very small. Yet this frequency is high enough to insure that galactic radiation is negligible, except near the galactic disk.

The radiometer used a transistor preamplifier and had a bandwidth of 1.5 Mhz centered at 1415 Mhz. The rectified output was recorded on a chart recorder, with the response time of the system determined by the settling time of the pen, ~ 0.5 second. The antenna was pointed at an elevation of 32° and

an azimuth of 226° , because a continuously operated 16-Ghz radiometer system oriented in this direction is located approximately 200 m north of our antenna. The 16-Ghz device is part of a system that monitors antenna temperature to obtain atmospheric attenuation statistics at that wavelength.

Observations were made on ten occasions for periods ranging from 24 to 100 hours, during rainy weather. The data included some two dozen heavy rainstorms as well as a number of extended periods of light rain. In no case did the antenna temperature increase during a rainstorm exceed $5^\circ K$ (3), a value an order of magnitude below the predictions mentioned above. Small increases, typically $1^\circ K$ to $2^\circ K$, were observed, however. When these features were compared with the attenuation at 16 Ghz derived from the noise data, good correspondence of features was obtained. The ratio of the equivalent attenuation at 1415 Mhz (that is, the observed increase in antenna temperature divided by $280^\circ K$) to the attenuation at 16 Ghz, was typically 2×10^{-3} for heavy rainstorms (Fig. 1).

The sharp spikes on the 1415-Mhz

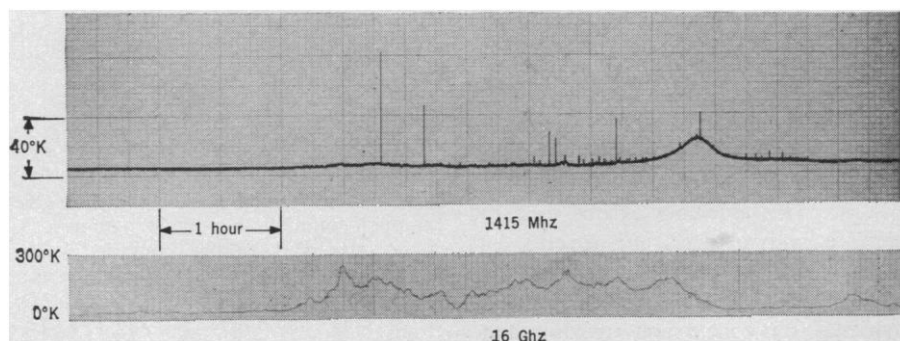


Fig. 1. Radiometer records at 1415 Mhz and 16 Ghz. Small but definite increases in the upper trace coincide with peaks in the lower record.

record (Fig. 1) are due to lightning strokes. (Although perhaps ten times as many appear on some of our records, their integrated energy never exceeded a small fraction of a degree of antenna temperature.) The large deflection on the 1415-Mhz record is due to the passage of the plane of the galaxy through the antenna beam as the earth rotates. Its daily presence on the records provided a convenient check of our sensitivity and timekeeping. (At 16 Ghz this effect is undetectably small, given the sensitivity of our equipment.)

Although the observed increases in 1415-Mhz antenna temperature are clearly not of the magnitude predicted (1), the fact that any effect appears on the record is not otherwise easily accounted for (3). Indeed, standard calculations of attenuation by rain at 1415 Mhz lead to antenna temperature changes of only a small fraction of a degree (4). Such a calculation gives 5×10^{-4} for the ratio of attenuation at the two frequencies or only about one tenth of the peak value observed. It is our conclusion that the observed effect, although not as high as the value

predicted by Sartor and Atkinson, does fall within the range of possible values discussed in their paper, given the uncertainty of the parameters upon which the calculations are based.

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References and Notes

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2. We thank D. C. Hogg who called this problem to our attention.
3. Two other possible ways of producing an increase in apparent system temperature correlated with rain rate were investigated and excluded. The first was accumulation of water on the waveguide window or walls of the antenna throat. Therefore, care was taken to make sure that critical components were kept free of water during observations. The second possible effect was rain scattering of man-made interference into our beam. Investigation of oscilloscope and chart records, on which spurious radar signals are normally readily discernible when present, failed to show evidence of such a signal. Furthermore, azimuthal scans along our horizon failed to reveal any interfering source.
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25 March 1970

Ice Sandwich: Functional Semipermeable Membrane

Abstract. At a temperature slightly below the freezing point of an aqueous solution, the functions of a nearly perfect semipermeable membrane can be simulated with two nonselective filters with ice sandwiched between them. Potential applications include production of potable water from brackish sources or of highly purified water from tap water.

Reflection on the process of frost heaving in soil revealed that an extraordinarily simple device should simulate the behavior of a nearly perfect semipermeable membrane. This device could have important applications in the purification of liquids, particularly water. Crude experiments showed that the device worked more or less as expected and suggested a configuration for optimum performance.

Functionally, the behavior of a semipermeable membrane for aqueous solutions can be simulated with a pair of rigid nonselective filters with ice maintained in a narrow space between (an "ice sandwich") held at a temperature slightly below the freezing point of the solution. This assembly can be used to simulate both osmosis and reverse osmosis. The ice phase provides the solute barrier, and its movement (engendered by concurrent freezing and melting at opposing faces in contact with the respective filters) provides for

solvent transport. The filters serve only as phase barriers, confining the ice phase to its allotted place even though supercooled water, or supercooled solution, fills the pores of the filters and adjoining spaces. The accompanying diagram depicts the system in schematic form (Fig. 1).

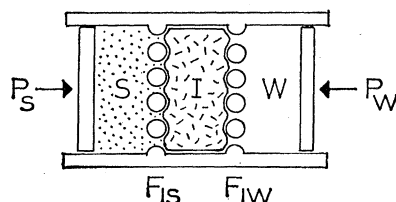


Fig. 1. The ice sandwich osmometer. One chamber contains an aqueous solution, *S*, at pressure P_S ; another contains water, *W*, at pressure P_W ; the intervening chamber contains ice, *I*, with the common walls being rigid filters, F_{IS} and F_{IW} . The osmometer is maintained at a temperature slightly below the freezing temperature of the solution.

The filters have two critical requirements. The first is that they be wettable by the liquid phase, with surface interactions that sustain a liquid film between the ice and the filter substance at subfreezing temperatures—a characteristic of common filter materials (and of soil particles). The second requirement concerns maximum pore size. Surface tension of the interface between ice and water tends to exclude ice from the filter pores at subfreezing temperatures, the maximum permissible pore size, r , depending upon the operating conditions. If, for example, the osmometer in Fig. 1 is at equilibrium, P_W is atmospheric pressure, P_S is adjusted to the osmotic pressure of *S*, and the temperature, T , is held below the freezing temperature of the solution, T_f ,

$$(r_{IS})_{\max} = \frac{2T\sigma}{d_w L(T_f - T)}$$

and

$$(r_{IW})_{\max} = \frac{2T\sigma}{d_w L(T_0 - T)} \approx \frac{5 \times 10^{-6}}{T_0 - T} \text{ cm}$$

where σ is the surface tension of the interface [30 dyne/cm is a good working value (1)], d_w is the density of water, L is the latent heat of fusion, and T_0 is the ice point. If the process is driven at a finite rate in either direction, these values shift slightly, reflecting local shifts of temperature, pressure, and concentration. Note that $(r_{IS})_{\max}$ is greater than $(r_{IW})_{\max}$.

A parameter of practical interest is the apparent permeability, k_w , of the ice sandwich. This is a complex quantity, but one can estimate its upper limit under the simplest possible circumstances, that is, when *S* and *W* are both pure water and a steady state has been established in which the limiting process is the transfer of the heat of fusion, L , across the ice layer of thickness l cm with this being the only heat transport (that is, the temperature on the high pressure side is uniformly higher than that on the low pressure side). We now write standard transport equations for the flow of water and heat, respectively, neglecting the impedance of the filters to water movement:

$$Q_w = k_w \frac{(P_S - P_W)}{l}$$

and

$$Q_h = k_h \frac{(T_S - T_W)}{l}$$

where Q_w is the mass of water transported per second per square centi-