

Temperature Effects on Conductivity of Seawater and Physiologic Saline, Mechanism and Significance

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Abstract

The conductivity of sea water and of 0.9% physiologic saline was examined as a function of temperature over a broad range. By inserting multimeter probes into samples prior to quick freezing, accurate resistance measurements were obtained even for the solid solutions at temperature below freezing. Data are also analyzed that suggest charge separation and charge density must be optimal for maximum conductivity of aqueous salt solutions. Ion mobility is not a requirement for conductivity. The data suggest a mechanism for electron transfer through salt solutions. The importance of saline and seawater differences is discussed.

Keywords: Conductivity; Density; Ion mobility; Electron transfer

Introduction

Aqueous salt solutions known as electrolytes are widely used in laboratory exercises with light fixtures to test for electrical conductivity of solutions under various conditions [1]. Although it is typically thought that mobile ions in solution somehow allow electron charge transfer through the solution, the detailed mechanism of how an electrolyte solution can complete an electric circuit is not clear. For example, solid sodium chloride contains sodium and chloride charged ions but is not a conductor. Dissolved sodium chloride aqueous solutions are conductors, even when the solution is frozen solid. This suggests that an optimum separation of cation and anion charge throughout the solution is required for conductivity, but the precise role of Brownian motion or ion mobility, with any presumed net migration of ions, has not been demonstrated. Although migration of ions is often mentioned as being involved, any buildup of charge separation in the solution is inconsistent with the fact that conduction of electrons supplied from an outside source is fully stable indefinitely. Unlike electrolytic or voltaic cells where oxidation reduction reactions take place and limit operation time, electrolyte solutions complete an electric circuit as does a wire, where electron migration takes place without any such chemical reaction.

Conductivity meters available retail typically cannot measure aqueous solution conductivity at temperatures below freezing due to difficulties with electrode design. This may partly explain why a paucity of data exists on conductivity of salt solutions at temperatures significantly below freezing. We here employ a resistance measuring multimeter with detachable electrodes to calculate the conductivity of solutions below freezing. The frozen electrolyte solutions exhibit significant conductivity with temperature dependence opposite that for liquid solutions. The data together indicate that ion charge separation is required for conductivity in electrolyte solutions but ion mobility is not.

Methods

Conductivity (κ) was measured in seawater over a temperature range below and above freezing. Seawater was collected in a 10 ml plastic cylindrical sample holder at the Scripps Institution of oceanography shoreline. The fluoride concentration was measured with a fluoride specific electrode and found to be 1.0 ppm, typical for open, undiluted seawater [2]. Temperature was measured with a laser guided infrared thermometer (Radio Shack Corporation, Fort Worth,

TX) for the initial quick frozen solid and the final room temperature. Due to liquid transparency, solutions were run in parallel containing an inserted thermometer for additional calibration of temperatures. Conductivity was calculated from ohms resistance R measured with a multimeter (Anova, Model 3300, Radio Shack, www.IEquus.com). The detachable stainless steel electrodes were inserted into a sample and affixed to the container at a 5 cm separation distance. The assembly was quick frozen in a -20°C freezer as a single unit without being attached to the multimeter. After removal from the freezer, electrode leads were attached to the meter and resistance readings were recorded as the assembly warmed to ambient temperature. The entire temperature range of readings was repeated on separate days. Values are reported as calculated mSierverts/cm units, where conductivity $\kappa=1/\text{resistivity}$, after calibrating the resistance readings to known conductivity for salt solutions at 20°C recorded with a traditional conductivity meter. A 0.9% physiologic saline solution (purchased from Kendall McGaw Laboratories, Inc., Irvine, CA) was used to calibrate the system and also for additional conductivity measurements as a function of temperature. Data from the National Institute of Standards and Technology indicate a conductivity of $\kappa=14.5\text{ mS/cm}$ (and resistivity $\rho=68.9\text{ Ohm-cm}$) for a 0.9% saline solution at 22°C , which corresponded to a resistance of 76 Mohm in the experimental system employed here.

Results

A typical temperature dependence data set for seawater from -20 to 18°C is shown in Figure 1, where seawater freezes at -2°C . Conductivity for liquid seawater Figure 1B increases as a function of temperature over the range 0 to 30°C . The increase in conductivity is a linear dependence on temperature for the aqueous solution and compares to that published in tables which are charted in Figure 1C for comparison. Conductivity is also significant in frozen seawater,

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approximately 50,000 times that for frozen distilled water (Figure 1A). However, here conductivity decreases as a function of warming until the melting temperature is reached. The frozen solid salt water acts much like solid wire conductors, which exhibit decreased conductivity with increasing temperature [3]. The liquid salt solution exhibits increased conductivity with temperature which is the behavior of semiconductors, where electrons enter conduction bands as temperature increases. Ion mobility does not occur down a voltage gradient because the conduction in a salt solution (for either liquid salt solution or the solid) is permanent without change in magnitude as a function of time at a given temperature. Further, ion mobility is not required for conduction. But it is possible that Brownian motion in the liquid phase may modulate conductivity. Figure 1D presents data showing similar effects for 0.9% physiologic saline (0.154 M sodium chloride) which freezes at -0.6°C .

Discussion

The conductivity of seawater in the liquid phase at any positive Celsius temperature compares to that for seawater in the solid state at corresponding negative temperatures. The biphasic nature of conductivity surrounding the melting range is unique. The resistivity of seawater at 20°C (and at -20°C for frozen seawater) lies between that for the semiconductor silicon and for quartz and is comparable to that for Corning ware. The intrinsic resistivity for liquid seawater at 20°C is $\rho=RA/L=1.6 \times 10^6$ ohm-m (R resistance, A surface area for applied voltage field, L distance between electrodes). The temperature coefficient of resistivity is $\alpha=(\rho/\rho_0 - 1)/\Delta T=0.07$ ($^{\circ}\text{C}$) $^{-1}$. Both these values compare with those for semiconductors silicon and germanium [2,4].

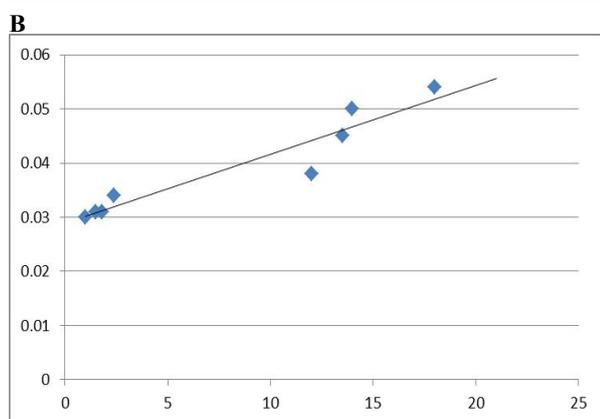
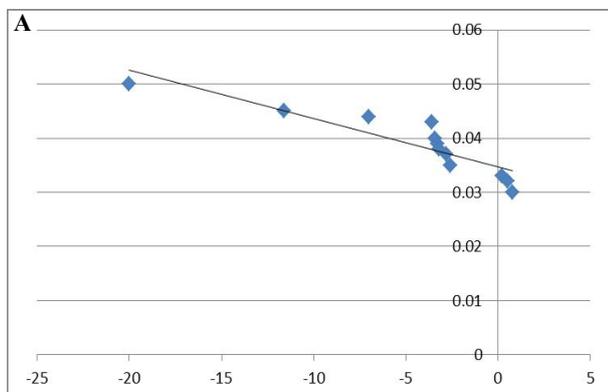


Figure 1A and 1B: Conductivity (Sieverts/cm) of seawater over the temperature range (A) -20 to 0°C and (B) 1 to 20°C .

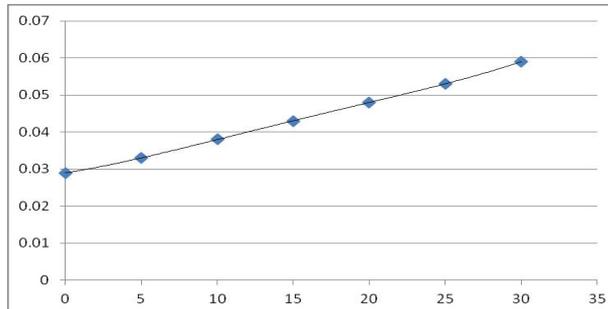


Figure 1C: Conductivity (S/cm) of seawater as a function of temperature over the range 0 to 30°C . Data are from ref. [2].

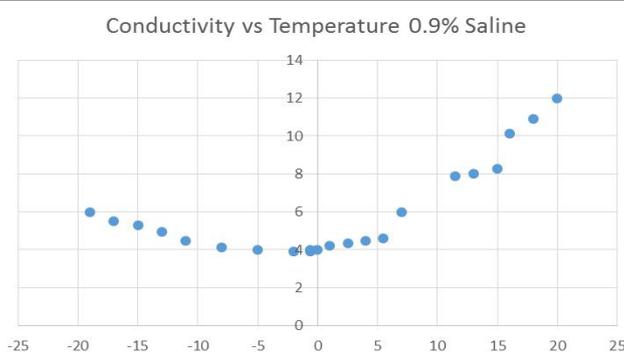


Figure 1D: Conductivity (mS/cm) of 0.9% sodium chloride as a function of temperature.

Pure water resistivity is very low and compares to that for glasses. The activation energy for the process of electron transfer in seawater was calculated from $E_a=R\ln(\rho_2/\rho_1)[1/T_1-1/T_2]=16$ kJ/mole. This compares to energies associated with molecular vibration and rotation. Vibration of molecules in the solid state is believed to interfere with electron flow as temperature increases. Liquid effects are more complex.

Sodium chloride solution conductivity also exhibits a U-shaped temperature dependence. One possibility is that conductivity of electrolyte solutions decreases in the solid phase with increasing temperature due to increased vibrational motion of water molecules, as has been proposed for vibration of atoms in solid wires. It is held in physics that rigid solids conduct better than agitated warmed solids. On the other hand, for the liquid phase, a commonly held notion in chemistry is that temperature increases in conductivity are caused by increased motion of molecules. As for solids, this interpretation appears unlikely in liquids since no significant increase in conductivity was detected for the electrolyte solutions as melting progressed to form increased proportions of liquid to solid phases at a fixed temperature. Also, directly inserting test leads into solid and then into liquid regions at the melting temperature point did not detect significant conductivity differences. Therefore, molecular motion in the liquid phase, that is not present in the solid phase, does not alter conductivity. Real temperature increases appear to be required to increase conductivity in the liquid phase from application of heat. Increased heat content alone does not affect conductivity at the melting point temperature. It may thus be intermolecular electron transfer, rather than molecular agitation, that rate-limits conductivity in liquids. Within compact solids however, it remains possible that atomic or molecular vibration due to warming inhibits conduction, where interatomic or intermolecular electron transfer is not as limited as it is in the liquid phase.

Conductivity measurements reported for salt solutions of varying cation radii and charge as a function of temperature and concentration are plotted in Figures 2-5. Ionic radii increase from Period 2 through Period 5 alkali elements where $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$ and alkaline earth elements where $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$ while radii are comparable for each period pair. This suggests that although electrons are attracted to cationic charge, the larger the ion, with less charge density over a larger surface area which does not retain attracted electronic charge, supports electron transfer in solution and thus higher conductivity.

Electron flow through the salt solution is required to complete a circuit, where electrons, not ions, must enter one electrode and be supplied from the other. Both frozen and liquid aqueous salt solutions remain constantly conductive. Thus, ion migration is not a necessary part of the conduction mechanism. Furthermore, in the absence of a redox reaction at any electrode, net ion migration under an applied electric field in the liquid phase cannot occur since this is prevented by diffusion down any concentration gradient so formed. However it is believed that conductivity increases with increasing cation diameter (Figure 2) may be due to increasing cation accessibility with decreased complexation water molecules that exists under the intense electric fields of the smaller cations [5]. For any Period of cation pairs having comparable radii, the conductivity appears to decrease for double positive charge compared to single positive charge. This suggests that electron attraction by the cation must not be too large in order to support electron transfer through a conductive aqueous solution. Data are from the CRC Handbook of Chemistry and Physics [2].

As seen from Figures 3 and 4 the 1 molal KCl solution at 10°C is 40,000 times more conductive than pure water at 10°C (0.008 mS/cm). A video demonstration of the effect freezing is available [6]. This indicates that ion mobility is not a requirement for electron transfer.

The molar conductivities of potassium chloride, bromide and iodide solutions were reported to be 107, 113, and 117 mS/cm-M [2]. For sodium chloride and bromide solutions the values are 82 and 90. Therefore any relationship between ionic radius of the halide anion and conductivity is much less significant than for radius changes of cations, where a 100% increase in conductivity occurred for potassium chloride compared to sodium chloride (Figure 2). This cation size effect however is less pronounced for nitrate salts, where molar conductivity values for potassium nitrate and sodium nitrate are 96 and 80 mS/cm-M.

At modest voltages as discussed in this analysis, a tungsten bulb lights for an electrolyte solution. But such a system is neither an electrochemical cell nor an electrolytic cell, since H_2 , O_2 , Na(s) , or Cl_2 are not produced during electron flow through the solution. Neither pure water in the absence of dissolved salt nor solid sodium chloride in the absence of water are conductors. It is possible that separated Na^+ cations in the polar solution act like catalysts that allow electron transfer from the anode to the cathode under the influence of the applied voltage. Electron transfer, from partially negative charged oxygen atoms on polar water molecules into the positive electrode, occurs only because electrons can be transferred from adjacent water molecules which are replaced with electrons from additional water molecules, which are replaced with electrons transferred from the anode to prevent depletion of electrons. This occurs under the influence of the attracting positive charged sodium cations while maintaining an unchanged overall neutral solution.

The idea that electrolyte solutions are conductive because of net ion migration as written in chemistry texts only applies to high voltages that cause electrolysis or an oxidation reduction reaction in solution.

Ion migration is not involved in electronic conductivity of electrolyte solutions. Saline solutions are good conductors and exhibit significant conductivity even when the solution is frozen, in the absence of net migration of ions or any possible buildup of net charge. The frozen solution behavior compares to conduction along a metal wire where a sea of electrons drift due to an applied voltage without requirement for movement of atoms in the wire.

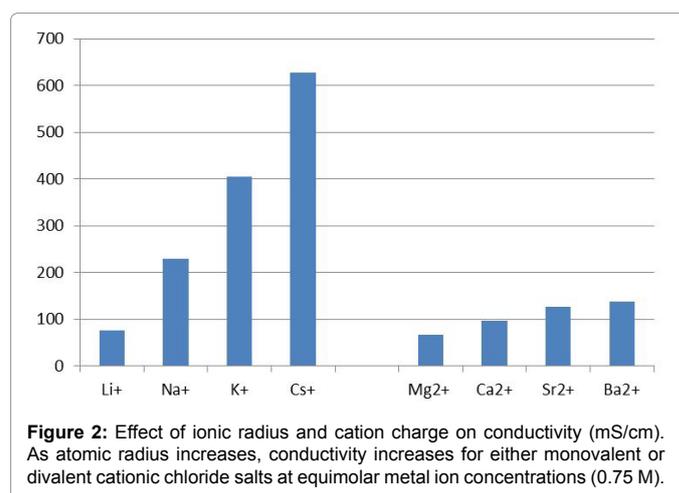


Figure 2: Effect of ionic radius and cation charge on conductivity (mS/cm). As atomic radius increases, conductivity increases for either monovalent or divalent cationic chloride salts at equimolar metal ion concentrations (0.75 M).

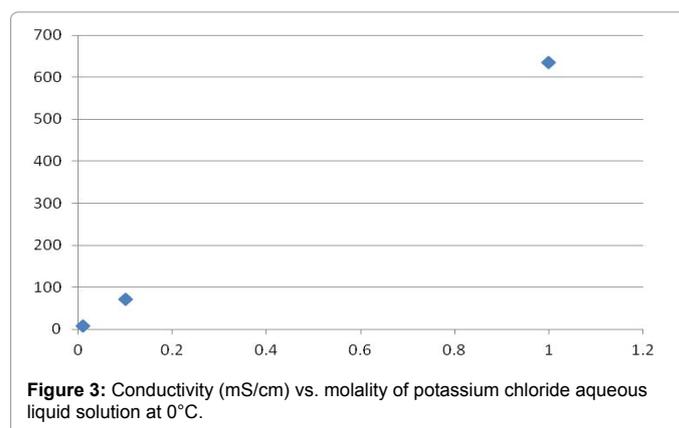


Figure 3: Conductivity (mS/cm) vs. molality of potassium chloride aqueous liquid solution at 0°C.

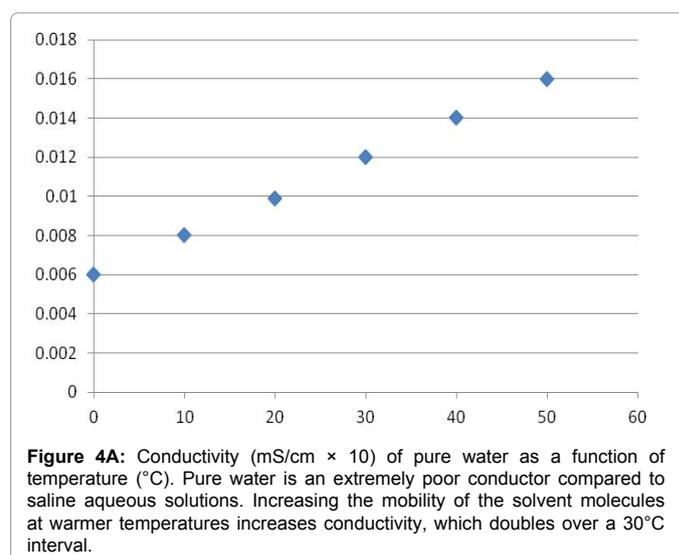
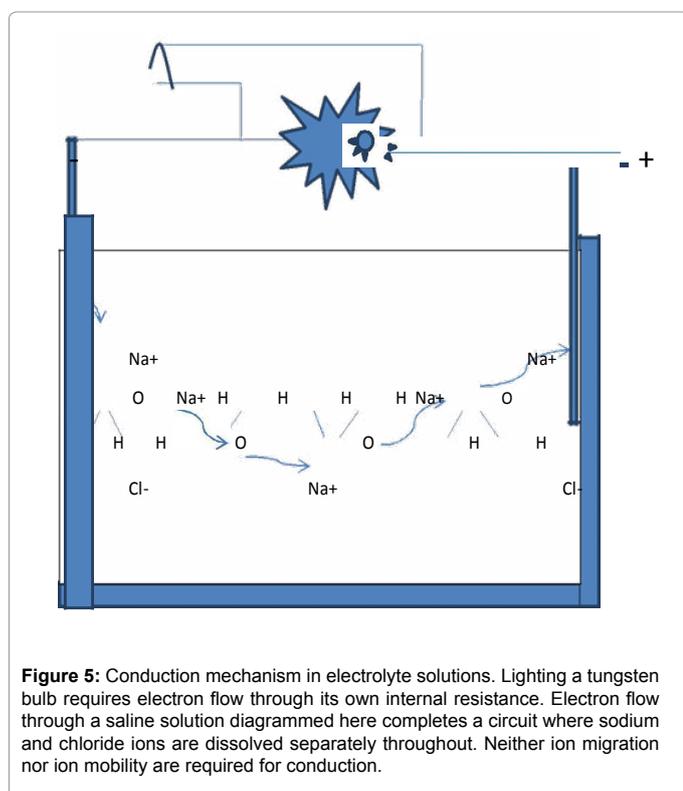
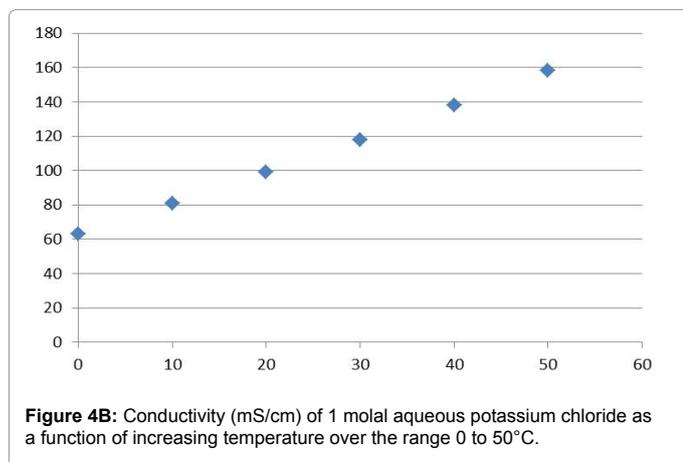


Figure 4A: Conductivity (mS/cm × 10) of pure water as a function of temperature (°C). Pure water is an extremely poor conductor compared to saline aqueous solutions. Increasing the mobility of the solvent molecules at warmer temperatures increases conductivity, which doubles over a 30°C interval.



Resistance of a liquid salt solution decreases with increase in temperature. Transfer of electrons can occur as long as the catalytic sodium ions are at an optimum distance of separation in a polar medium. Since water is 55 Molar and a 0.9% saline solution at 0.15 Molar exhibits substantial conductivity, the average distance of separation between sodium ions in this conducting solution may be estimated (approximately 95 nanometers). Since conductance $C (=1/\text{resistance } R)$ relates to conductivity $(=1/\text{resistivity } \rho)$ as $1/R=A/(L\rho)$, and $L=5$ cm in this system with $1/\rho=\kappa=14.5$ mS/cm and an observed conductance of $1/R=1/49.2 \times 10^6=2.0 \times 10^{-8}$ ohm⁻¹, the electron flow area region between electrode tips may be estimated at 7×10^{-6} m². If this conducting area were assumed to mimic a circular wire, the area corresponds to a diameter of 3 mm and a volume of 1 nL in this system. This interpretation is consistent with the fact that resistance readings were observed to be constant for any volume used in the system as long

as the volume was sufficient to cover the electrode tips, and knowing that electron flow follows the path of least resistance between points of differing voltage. Conduction takes place along the most direct path between the electrodes. Although the conduction band is not known to be cylindrical in shape as for a wire, this is a reasonable proposition here for the sake of argument.

A 1 nL volume for the estimated conduction band of a 0.9% sodium chloride solution requires approximately 11.5×10^6 water molecules at 260 pm diameter to cover a 3 mm diameter, with 192×10^6 molecules along a 5 cm length strand. At 0.15 M, an estimate of the number of sodium atoms of comparable diameter (0.15/55) (192×10^6) spread through the volume to cover this distance is approximately 5.2×10^5 , with a separation distance of roughly $0.05 \text{ m}/1 \times 10^{10}=95$ nm.

Molten sodium chloride also exhibits conductivity. The mechanism of electron flow through the mobile ions is unknown, but the distance between cations in the pure liquid salt would be greater than that for the ionically bonded solid. It is possible that anhydrous salts are conductive as melts, but nonconductive as solids, due to this separation of Na⁺ from Cl⁻ ions compared to that for the organized crystalline solid, rather than increased ion mobility *per se*.

The work presented here suggests that conductivity measurements could be used to distinguish between fresh water icebergs that break away from land glaciers into the sea, versus seasonal sea ice. A simple resistance multimeter should provide a reading for sea ice (on the 20 Mohm scale at 5 cm separation between electrodes), where brine content and thus conductivity would reflect the time since the ice formed. No resistance measurements would be detectable for fresh water icebergs.

Since the calcium concentration and alkalinity of seawater compare to that in the mammalian bloodstream, and seawater contains electrolytes that exist in blood, one theory often described is that life may have first originated through 'spontaneous generation' or 'chemical evolution' in seawater. This idea however is not consistent with the data presented here. The conductivity of seawater is nearly 4 times that for a 0.9% physiologic saline solution that is isotonic to extracellular fluid of living organisms. Also the sodium ion concentration of seawater (460 mM) is 70 times its concentration in cell cytoplasm (5-10 mM). Further, the calcium concentration of seawater (1.4 mM) is 14,000 times greater than for intracellular fluid (0.1 μM). Physiologic mM calcium in extracellular fluid can bind to membrane phospholipid phosphate groups, negatively charged at alkaline pH, to decrease/regulate the fluidity of the lipid bilayer [7,8]. But mM calcium inside cells is lethal, binds to negatively charged phospholipid moieties that predominate the inner half of the cell membrane, and generally denatures intracellular macromolecules. Amino acids and macromolecules can be formed from inanimate matter in the laboratory, but living cells, requiring very large ion concentration gradients across membrane surfaces, are electrolytically complex. As held by Isaac Newton, the mechanism by which a living organism first originated, which cannot be determined afterward with scientific experimentation, only the Lord knows.

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