Table 2. NaCl desorption from a mixed bed of ion-exchange resins by 0.15-percent calcium hydroxide (4.05 meq per 100 ml). The column originally was exhausted with a 3.62-percent NaCl solution in water.

Effluent (ml)	NaCl	
	Concentration (%)	Total removal (meq)
100	3.64	64.3
200	3.75	128.9
300	3.75	193.5
350	2.85	217.9
400	2.15	236.4
500	1.75	266.4

ml every 40 seconds. The effluent was collected on a fraction collector in 10-ml portions. Sodium was analyzed in the flame on a Beckman model B; and *p*H readings were taken to determine the presence of the OH^- ion, and hence the replacement of the chloride. The results of this experiment (Table 1) show an observed capacity of 805 milliequivalents (meq).

According to an often accepted generalization (*8*), 30 to 40 percent of the total column volume of 740 ml is void volume; this means that there is 296 ml of water in the system. At an input concentration of 3.62-percent NaCl, this volume is to be interpreted as a dilution by 185 meq. Hence the true capacity was 620 meq.

At the rated capacity of the column (1036 meq referred to calcium), the efficiency shown for the sodium-calcium exchange was 60 percent.

A mixed bed of cation- and anion-exchange resin was converted independently to the sodium and chloride forms by passage of a solution of 3.5-percent sodium chloride. A part of this solution was set aside for use in subsequent regeneration. Part of the exhausted resin (50 ml tamped volume) was transferred to a beaker by washing with a portion of the solution which was used to convert the resin into the sodium and chloride forms. Free-flowing water was drawn off by gentle tipping and rotating of the beaker. Thirty milliliters of a 5-percent slurry of calcium hydroxide, suspended in the 3.5-percent solution of sodium chloride that had been set aside, was then added to the decanted resin. The mixture was stirred for 5 minutes with a magnetic stirrer at low speed, with a Teflon-coated, football-shaped, stirring bar. Subsequently, the resin was allowed to settle and the supernatant liquid was analyzed by taking sodium readings in the flame.

The salt content of the supernatant liquid was 4.5 percent; this is equivalent to a concentration increase of 12.8 percent when the volume of the regenerant is 60 percent.

The anion-cation exchange column, exhausted by passage of the NaCl solution as in the initial experiment, was inverted and a solution of 0.15-percent calcium hydroxide, that is, 4.05 meq per 100 ml, was percolated downward. Samples were collected as already described.

The analytical results are given in Table 2. The total salt in the effluent from this regeneration amounted to 266.4 meq. The interstitial volume (at the most, 296 ml) was full of remaining liquid at the beginning of the regeneration; an interpolation of the preceding run's end phase indicates that the maximum concentration of salt in the interstitial liquid was 3.25 percent—the column thus contained 165 meq of electrolytes that were not taken up. The input of 104 ml of water of lime (to make up the 500 ml of the effluent) resulted in a further addition to 173.26 meq.

The difference between the effluent ionic load of 266.4 meq and the input of 173.26 meq shows the intervention of another desorbent—the deposit of the insolubilized portion of the counterionically evolved lime which, owing to the action of the solubilizing water, goes from the insoluble to the soluble form, and then proceeds to dissociate. The ion-exchange resin takes up the available ions, causing a shift in equilibrium; and more hydroxide then dissolves and dissociates. These experiments point to the availability of the interstitially deposited lime for regeneration without physical handling.

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Chlorine Pentafluoride

Abstract. *The bonding in the halogen polyfluorides is similar to that in the xenon fluorides. Since* XeF_4 *exists, the previously unreported* ClF_5 *should exist. This compound has been prepared by heating* ClF_3 *in the presence of fluorine at high pressure. Chlorine pentafluoride is a square pyramidal molecule. It has a lower melting point than* ClF_3 *and a higher vapor pressure. It is also less reactive than* ClF_3.

Descriptions of the bonding in the xenon compounds have been of two different kinds. One involves a covalent-ionic resonance, the other primarily covalent bonding, but with *d* electrons involved. One of the minor difficulties with both descriptions is that they apply as well to the unreported compound ClF_5 as they do the xenon compounds (*1*).

The compound ClF_5 has now been successfully prepared by the combination of chlorine trifluoride and fluorine at high temperatures and with high fluorine pressures. Typically, a 14:1 mixture of F_2 and ClF_3 has been heated to 350°C for 1 hour at a pressure of about 250 atm (*2*).

The infrared spectrum of ClF_5 is similar to the spectra of BrF_5 and $XeOF_4$, indicating that ClF_5 has the same square pyramidal configuration with the chlorine atom nearly in the plane of the four fluorine atoms forming the pyramid base. The asymmetric stretching vibration, ν_7, involving the four fluorine atoms, corresponds to a very strong band at 732 cm^{-1}. The stretching vibration, ν_1, involving the apex fluorine atom, corresponds to a weaker but still strong band at 786 cm^{-1}. The symmetric stretching vibration involving the four fluorine atoms, ν_2, at 544 cm^{-1} is very weak compared with ν_7, indicating the bond angles are close to 90°.

The identification of ClF_5 has been verified in the mass spectrometer. Samples free of ClF_3 have not yet been prepared. A sample thought to contain a few percent ClF_3 is a white solid at liquid nitrogen temperature and a clear white or pale yellow liquid at −100°C. Similar samples have had a vapor pressure three- to fivefold greater than that of ClF_3. In sharp contrast with the behavior of ClF_3, ClF_5 reacts slowly, if it reacts at all, with water vapor.

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References and Notes

1. K. S. Pitzer [*Science* **139**, 414 (1963)], in discussing the bonding in the xenon fluorides and halogen fluorides, notes that detailed calculations indicate that the boundary of stability is essentially the same for the XF_4 units and XF_2 units where X represents, for example, xenon or ClF. He suggested that the F-F nonbonded exchange repulsions may account for the absence of a stable ClF_5.
2. The method was similar to that used in the preparation of XeF_6 by Dudley, Gard, and Cady [*Inorg. Chem.* **2**, 228 (1963)].

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Volume Changes of a Thixotropic, Sodium Bentonite Suspension during Sol-Gel-Sol Transition

Abstract. *Dilatometric measurements during the sol-gel-sol transition of an air-free, thixotropic, sodium bentonite suspension revealed a reversible change in volume of about* 2.4×10^{-4} *percent. The volume of the suspension increased during gelation and decreased when the gel was subsequently liquified. This is taken as evidence of a progressive building up, during gelation, of a water structure less dense than normal.*

Some colloidal systems stiffen to a gel on standing but become liquified again when disturbed by stirring or vibration; systems exhibiting this behavior in a reversible manner under virtually isothermal conditions are said to be thixotropic. There has been speculation and debate over the nature of the gel state and its source of strength. Most investigators now regard the gel as a more or less continuous framework made up of the solid phase, the interstices being passively occupied by the suspending liquid (*1*). But the extent, however small, to which the suspending fluid is affected by the solid phase during the gelation of colloidal suspensions is no doubt important in physical and biological systems (*2*, *3*).

In bentonite clay suspensions, for example, it is known that water in close proximity to the mineral surfaces is significantly influenced by the solid phase; its density is lower than that of normal water (*4*), its viscosity is higher (*5*), and the ionic mobilities and diffusion coefficients of solutes in it are lower (*6*) than in aqueous solution. Moreover, as thixotropic bentonite suspensions gel, all of the water is affected (*7–9*). The chemical potential of the water decreases gradually as gelation proceeds but is nearly restored to its initial value when, upon agitation, the suspension is reliquified (*9*).

One is thus led to visualize the sol state as a suspension of clay particles oscillating in Brownian motion, about which a water structure, less dense than normal but of limited extent, has been induced. As gelation proceeds the particles contact each other and orient themselves into a continuous network; as this happens their Brownian motion ceases or is greatly reduced, promoting a more extensive development of the water structure. If this is true and if the induced water structure is less dense than that of normal water, an increase in the volume of the suspension is to be expected upon gelation, followed by a decrease in volume on subsequent liquefaction of the gel.

To test this prediction we measured the volume changes accompanying the sol-gel-sol transformation of a thixotropic, sodium bentonite suspension by means of a sensitive dilatometer. The dilatometer was a U-tube made by fusing together two lengths of glass tubing. One arm was simply a length of glass capillary (0.6 mm inner diameter) and the other consisted of a length of glass tubing (15.0 mm inner diameter) with a glass stopcock at the top. The latter was cut so that its volume was about 75 cm³. During the construction of the dilatometer, a stainless-steel ball measuring 12.8 mm in diameter was sealed in the large arm.

A sodium bentonite suspension was prepared by slowly passing a dilute (about 20 g clay per liter) suspension of Wyoming bentonite through a sodium-saturated, Rohm and Haas IR-120 cation-exchange resin (*10*). The resulting suspension was concentrated to 4.67 g per liter by evaporation and placed in a large vacuum erlenmeyer flask (*7*). Preliminary experiments showed that the presence of occluded air resulted in an initial irreversible volume change on gelation that appeared to depend upon the amount of air present and the method employed in filling the dilatometer. Apparently, this effect has not been recognized before (*11*). To remove as much occluded air as possible, the suspension was agitated for half an hour during which time it was exposed to the partial vacuum created by a water aspirator. The suspension was then drawn into the dilatometer and confined between the closed stopcock at the top of the large arm and a 10-cm thread of mercury in the capillary tube. Care was taken to insure that no air was entrained while the dilatometer was being filled. The height of the interface of the mercury and suspension was adjusted during filling so that a slight positive hydrostatic pressure was created throughout the suspension. The filled dilatometer was then put into a water bath maintained at constant temperature (30° ± 0.005°C); the steel ball was raised and kept in position at the top of the dilatometer with a magnet. The position of the interface was then observed periodically through the telescope of a cathetometer.

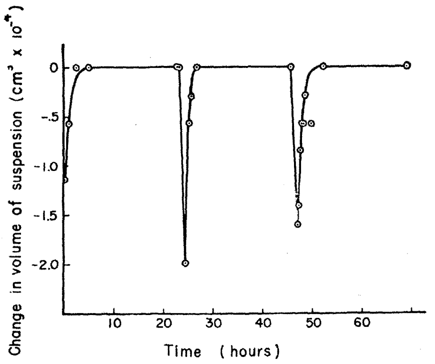

Fig. 1. The change in the volume of a suspension during three sol-gel transitions as a function of time.

After a certain time the steel ball was released, and the time taken for it to fall through the suspension was measured. The ball was raised immediately afterwards and was allowed to fall again; this was repeated 25 or 30 times until the time being taken for it to fall through the suspension was constant. Timing the falling steel ball gave an index of the strength of the gel and the repeated passage of the ball through the tube provided a means of liquifying the gel at will. The gel strength, as inferred from the initial falling time of the steel ball, increased noticeably as the time interval between the initiation of gelation and release of the ball was progressively lengthened, increasing more than threefold during the first hour. After an interval of 24 hours, the times taken for the