mann constant, R the gas constant, $\mathfrak{F}$ the Faraday constant, and T the absolute temperature.

If we express λ_j^0 in (coulomb/sec.) (cm.^{2}/volt), $\mathfrak{F}$ in coulombs, R in joules per ° C. per mole, and replacing n_i by c_i which denotes concentration in moles per liter, equation (1) can be written as

$$D_j = \frac{RT\lambda_j^0}{|Z|\mathfrak{F}^2} - \frac{\lambda_j^0|Z_j|\mathfrak{F}}{3N\mathfrak{D}} \times$$
$$2.694 \times 10^{16}\sqrt{\frac{4\pi}{\mathfrak{D}RT}}\,[1 - \sqrt{d(\omega_j)}]\,\sqrt{\sum_i c_i Z_i^2} \quad (8)$$

For the diffusion of tracer amounts of radioactive ions of chemical species No. 1 in salt solution containing non-radioactive ions of chemical species No. 1 and No. 2, we have

$$c_1|Z_1| = c_2|Z_2| \quad (9)$$

For uni-univalent electrolyte $|Z_1| = |Z_2| = 1$, and equation (3) can be written as

$$d(\omega_1) = \frac{1}{2}\left[\frac{1}{2} + \frac{\lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right] \quad (10)$$

If we take $\lambda_1^0 = 50.11$ for the sodium ion and $\lambda_2^0 = 76.36$ for the chloride ion[10] at 25°, equations (8) and (10) can be combined to give

$$D \times 10^5 = 1.334 - 0.268\sqrt{c} \quad (11)$$

for the diffusion of tracer amount of radioactive sodium ion in aqueous sodium chloride solutions at 25°.

The self-diffusion coefficients of sodium ion in aqueous sodium chloride solutions at 25° listed in Table I are plotted *vs.* the square root of concentration in Fig. 1. The straight line in the dilute concentration region represents equation (11) according to Onsager's theory. Figure 1 indicates that the measured self-diffusion coefficients agree with the values predicted by the Onsager equation within experimental uncertainty at concentrations below 0.04 formular-weight per liter. Above 0.05 formular-weight per liter the self-diffusion coefficient increases with increasing salt concentrations, reaches a maximum value near 0.4 formular-weight per liter and then starts again to decrease with increasing salt concentration. The general shape of the present D *vs.* $\sqrt{c}$ curve resembles that for the diffusion of tracer amount of sodium ion in aqueous potassium chloride solution, but the peak of the D *vs.* $\sqrt{c}$ curve obtained in the present work appears at $c = 0.4$ instead of at $c = 1.3$ for the diffusion of tracer amount of sodium ion in aqueous potassium chloride solution. A possible explanation is given below.

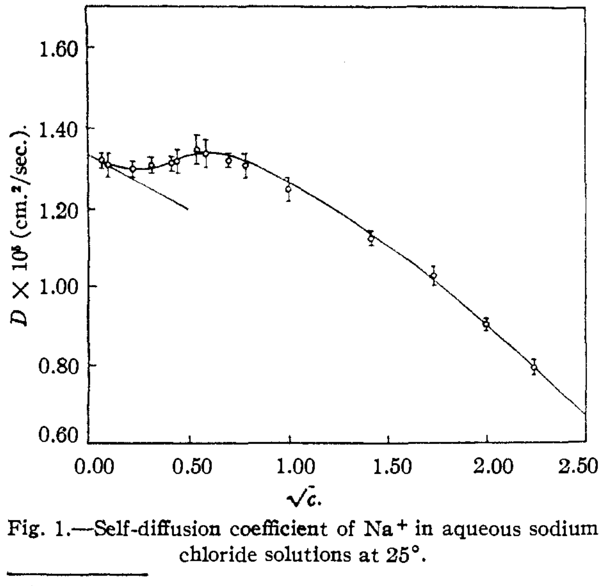

Fig. 1.—Self-diffusion coefficient of Na$^+$ in aqueous sodium chloride solutions at 25°.

In an aqueous potassium chloride solution containing tracer amount of sodium ion, the potassium ions, because of their smaller radii, tend to have closer association with chloride ions than the tracer amount of sodium ions. Consequently the nearest chloride ions surrounding each sodium ion are pulled away from the sodium ion by the potassium ions. Because of this effect the average center to center distance between each of the tracer amount of sodium ions and its nearest chloride ions in aqueous potassium chloride solution becomes larger than the corresponding distance in a pure sodium chloride solution of the same chemical concentration. Consequently, the forces that produce the maximum in the D *vs.* $\sqrt{c}$ curve for the tracer-diffusion of sodium ion in potassium chloride solution should come into play and produce a similar effect on the shape of D *vs.* $\sqrt{c}$ curve for the self-diffusion of sodium ion in sodium chloride solution at a more dilute concentration. The large difference between the two concentrations at the maxima of the two D *vs.* $\sqrt{c}$ curves is not too startling because for a given directional distribution of ions, the average distance between nearest neighbors varies inversely with $c^{1/3}$. However, in view of the complexity of the present problem, it appears unlikely that a quantitative correlation of these two concentrations can successfully be made before a satisfactory theory of liquid water has been formulated.

Acknowledgment.—In preparing the present work the authors have benefited by discussion with Professor H. S. Harned. A research fellowship granted by the du Pont de Nemours Co. to one of us (J. H. W.) is gratefully acknowledged.

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Tracer-diffusion in Liquids. III. The Self-diffusion of Chloride Ion in Aqueous Sodium Chloride Solutions

BY JUI HSIN WANG

The self-diffusion coefficients of chloride ion in aqueous sodium chloride solutions at 35° have been determined by Jehle.[1] However, extrapolation of Jehle's values yields a limiting tracer-diffusion coefficient at infinite dilution for chloride ion which is almost 20% higher than Nernst's limiting value as calculated from conductance and transference data. In view of the extensive work done by Harned and

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[10] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1950, Appendix A.

[1] L. Jehle, Ph.D. Thesis, University of California, Berkeley, 1938.

co-workers[2] in the past few years, it is extremely unlikely that Nernst's limiting relationship can be wrong. Furthermore, the shape of the diffusion coefficient *vs.* concentration curve obtained by Jehle showed close resemblance to that for salt diffusion which exhibits rapid increase of diffusion coefficients with salt concentration at high concentrations. This increase in salt diffusion coefficient at high salt concentrations is primarily due to the variation of the activity coefficient of the diffusing salt along the path of diffusion. Since in tracer-diffusion the activity coefficient of the diffusing tracer ion is practically constant along the diffusion path, we can only infer that the mobility of chloride ion in aqueous sodium chloride solution continues to increase with increasing salt concentration even at 2 molal if Jehle's result is to be accepted. Such a conclusion, if accepted, would invalidate the picture adopted to explain the concentration dependence of the tracer-diffusion coefficients of sodium ion in aqueous potassium chloride[3] and sodium chloride[4] solutions. Since Jehle's work appears to be the only piece of experimental work that has been done on the tracer-diffusion of chloride ion, it seems desirable to redetermine the tracer-diffusion coefficients of chloride ion by the improved capillary technique. In the present work the self-diffusion of chloride ion in aqueous sodium chloride solutions has been measured with Cl^{36} as tracer.

Experimental

The Cl^{36} used was obtained from the Isotopes Division of U. S. Atomic Energy Commission at Oak Ridge, Tennessee. The Cl^{36} was originally shipped in the form of hydrochloric acid solution. This was converted to dry sodium chloride before being used to prepare radioactive sodium chloride solutions. The diffusion apparatus and manipulations have already been described in Paper I[3] of this series.

Results

The measured self-diffusion coefficients of chloride ion in aqueous sodium chloride solutions of various concentrations at 25.00° are listed in Table I.

TABLE I

SELF-DIFFUSION COEFFICIENTS OF Cl^- IN NaCl(AQ.) AT 25°

Concn. of NaCl soln., formular-wt. per l.	$D \times 10^5$, cm.²/sec.	Concn. of NaCl soln., formular-wt. per l.	$D \times 10^5$, cm.²/sec.
0.030	1.975 ± 0.015	1.000	1.77 ± 0.016
.050	1.96 ± 0.04	2.000	1.61 ± 0.03
.100	1.94 ± 0.024	3.000	1.44 ± 0.035
.250	1.91 ± 0.025	4.000	1.24 ± 0.015
.500	1.85 ± 0.04	5.000	1.06 ± 0.03

Each value listed in Table I is the average result of three or four measurements. The standard deviation varies from 2.6% for 3.000 molal to 0.75% for 0.030 molal concentration. Measurement of the self-diffusion coefficient of chloride ion in sodium chloride solution below 0.03 molal concentration became tedious because of the low specific activity of Cl^{36} used, and was therefore not attempted.

Discussion

When appropriate units are used, the Onsager equation[5] can be written as[3,4]

$$D_j = \frac{RT\,\lambda_j^0}{|Z_j|\,\mathfrak{F}^2} - \frac{\lambda_j^0\,|Z_j|\,\mathfrak{F}}{3N\,\mathfrak{D}} \times$$

$$2.694 \times 10^{16} \sqrt{\frac{4\pi}{\mathfrak{D}\,RT}}\,[1 - \sqrt{d(\omega_j)}]\,\sqrt{\sum_i c_i Z_i^2} \quad (1)$$

where for the diffusion of tracer amount of radioactive ions of chemical species No. 1 in salt solution containing non-radioactive ions of chemical species No. 1 and No. 2

$$d(\omega_1) = \frac{1}{2}\left[\frac{1}{2} + \frac{\lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right] \quad (2)$$

If we take $\lambda_1^0 = 76.36$ for the chloride ion and $\lambda_2^0 = 50.11$ for the sodium ion,[6] we obtain from equations (1) and (2)

$$D \times 10^5 = 2.033 - 0.526\sqrt{c} \quad (3)$$

for the self-diffusion coefficient of chloride ion in aqueous sodium chloride solutions at 25°. Values of self-diffusion coefficients of chloride ion in aqueous sodium chloride solutions at 25° listed in Table I are plotted *vs.* the square root of concentration in Fig. 1. The straight line in the dilute concentration range represents equation (3). Although in the present work it has not been possible to make measurements below 0.03 formular-weight per liter in concentration because of the limited specific activity of radioactive chlorine used, it appears from the diagram that as the concentration of the solution approaches zero measured diffusion coef-

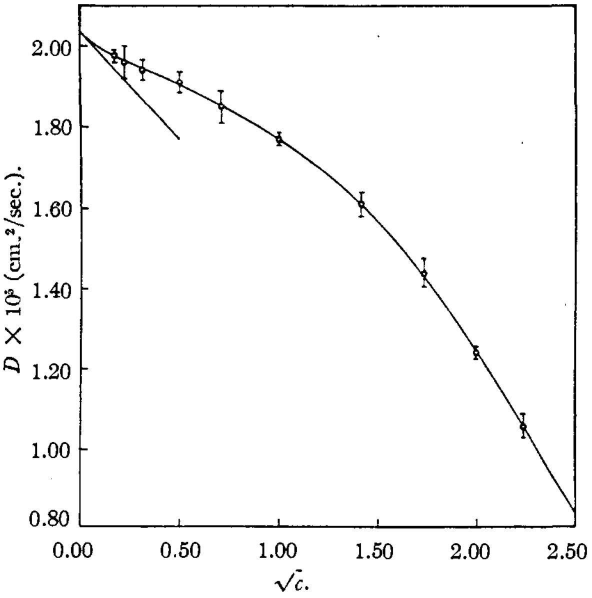

Fig. 1.—Self-diffusion coefficient of Cl^- in aqueous sodium chloride solutions at 25°.

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[2] H. S. Harned and D. M. French, *Ann. N. Y. Acad. Sci.*, **46**, 267 (1945); H. S. Harned and R. L. Nuttall, THIS JOURNAL, **69**, 736 (1947); *ibid.*, **71**, 1406 (1949); H. S. Harned and A. L. Levy, *ibid.*, **71**, 2781 (1949); H. S. Harned and C. A. Blake, *ibid.*, **72**, 2265 (1950); *ibid.*, **73**, 2448 (1951); *ibid.*, **73**, 4255 (1951); H. S. Harned and C. L. Hildreth, Jr., *ibid.*, **73**, 650 (1951); *ibid.*, **73**, 3292 (1951); H. S. Harned and R. M. Hudson, *ibid.*, **73**, 652 (1951); *ibid.*, **73**, 3781 (1951); *ibid.*, **73**, 5083 (1951).

[3] J. H. Wang, *ibid.*, **74**, 1182 (1952).

[4] J. H. Wang, *ibid.*, **74**, 1611 (1952).

[5] L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).

[6] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1950, Appendix A.

ficient approaches Nernst's limiting value of 2.033 × 10^{-5} cm.^{2}/sec. at infinite dilution. In contrast to Jehle's values for the self-diffusion of chloride ion in aqueous sodium chloride solutions at 35°, the D *vs.* $\sqrt{c}$ curve obtained in the present work shows that the self-diffusion coefficient of chloride ion continues to decrease with increasing salt concentration in the range between 0.03 to 5.00 formular-weight per liter.

It is also seen from Fig. 1 that in contrast to the D *vs.* $\sqrt{c}$ curves for the diffusion of tracer amount of sodium ion in aqueous potassium chloride and sodium chloride solutions, respectively, the D *vs.* $\sqrt{c}$ curve obtained in the present work does not possess a maximum in the whole concentration range studied. This absence of maximum for the D *vs.* $\sqrt{c}$ curve for the tracer-diffusion of chloride ion does not, however, contradict the qualitative explanation suggested earlier[3] if the effect of size of hydrated ion is taken into consideration.

It has been pointed out[7] that the degree of "distortion" that exists in the semi-crystalline structure of "solvent" water in the immediate neighborhood of a hydrated ion seems to increase with decreasing size of the hydrated ion. If this is true, the degree of "distortion" in the structure of solvent water immediately surrounding a smaller chloride ion at infinite dilution should be larger than that for a larger sodium ion. Consequently as the salt concentration increases the increase in the degree of distortion (*i.e.*, the distortion due to finite salt concentration in addition to the distortion that already exists at infinite dilution in the structure of the immediately surrounding solvent water molecules) and, hence, the increase in self-energy should be smaller for chloride ion than for sodium ion in the same sodium chloride solution at moderate concentrations. Since it is the increase in self-energy, as concentration increases, rather than the absolute value of self-energy that makes the tracer-diffusion coefficient increase with increasing salt concentration, it is clear that we should expect Hückel's saturation effect to be smaller for chloride ion than for sodium ion in the same solution at moderate concentrations. Accordingly we should expect the peak in D *vs.* $\sqrt{c}$ curve to be less pronounced for the chloride ion than for the sodium ion which is not in disagreement with the curves obtained experimentally.

The fact that at infinite dilution the degree of distortion that exists in the structure of solvent water in the immediate neighborhood of a hydrated ion increases with decreasing size of the hydrated ion is clearly demonstrated by computing the activation energy for tracer-diffusion of various ions at infinite dilution. If we assume that the activation energy, E, for tracer-diffusion can be calculated by

$$-E/R = \mathrm{d}(\ln D)/\mathrm{d}(1/T) \qquad (4)$$

and that at infinite dilution D is given by equation (1) as

$$D = RT\,\lambda^0/|Z|\,\mathfrak{F}^2 \qquad (5)$$

we may calculate the activation energy for tracer-diffusion from conductance data by

$$E/R = -\,\mathrm{d}[\ln (T\,\lambda^0)]/\mathrm{d}\,(1/T) \qquad (6)$$

Individual ionic conductances at infinite dilution for the alkali and halide ions between 5 and 55° have been accurately measured.[6,8] The activation energies for the tracer diffusion of several ions in their aqueous solution at infinite dilution calculated by means of equation (6) from these conductance data are listed in Table II.

TABLE II

ACTIVATION ENERGY FOR TRACER-DIFFUSION OF SEVERAL IONS IN INFINITELY DILUTE AQUEOUS SOLUTION AT 25°

Ion or molecule	E, kcal./mole	Ion or molecule	E, kcal./mole
Li^+ (aq.)	4.56	Cl^- (aq.)	4.17
Na^+ (aq.)	4.39	Br^- (aq.)	4.07
K^+ (aq.)	3.99	I^- (aq.)	4.05
Rb^+ (aq.)	3.95	H_2O	4.6
Cs^+ (aq.)	3.86		

Values in Table II show that as the size of hydrated ion increases from Cs^+(aq.) to Li^+(aq.), the activation energy for tracer-diffusion increases and approaches that for the self-diffusion of pure water. This tendency indicates that the actual activation mechanism for tracer-diffusion of various ions in infinitely dilute aqueous solution probably involves the activation of the immediately surrounding solvent water molecules to get out of the way of the tracer-ion. Since the self-diffusion and viscous flow in pure liquid water involve essentially the same activation mechanism,[9] values in Table II also indicate that when the size of the hydrated diffusing molecule becomes large as compared to water molecules its mobility D/RT should be inversely proportional to the viscosity of solvent water, a relationship that is well known in the case of large spherical molecules as Stokes' law. The fact that the smaller hydrated ions have smaller activation energy for tracer-diffusion than for the self-diffusion or viscous flow of pure water is a microscopic analog of the "slip" phenomena in viscosity measurements.

It may also be noticed from Table II that the activation energy for the tracer-diffusion of the halide ions also increases with increasing size of ion. However, since the water molecule is not symmetrical with respect to polarity, direct comparison of the activation energies for the tracer-diffusion of anions with that of the cations is difficult.

A remark on the definition of activation energy as

$$E = -R\mathrm{d}\,(\ln D)/\mathrm{d}(1/T) = -R\mathrm{d}[\ln (\lambda^0 T)]/\mathrm{d}\,(1/T)$$

instead of simply as $E = R\,\mathrm{d}\,(\ln \lambda^0)/\mathrm{d}\,(1/T)$ seems desirable. If we accept Eyring's transition-state theory of rate processes for tracer-diffusion in dilute aqueous solutions, the tracer diffusion coefficient D is given by

$$D = \lambda^2 \left(\frac{kT}{h}\right)\left(\frac{f^{\ddagger}_{\mathrm{trans}}}{f_{\mathrm{trans}}}\right)\left(\frac{f^{\ddagger}_{\mathrm{rot}}}{f_{\mathrm{rot}}}\right)\left(\frac{f^{\ddagger}_{\mathrm{vib}}}{f_{\mathrm{vib}}}\right) e^{-E/RT} \qquad (7)$$

where λ is a constant characteristic of the system under consideration and reduces to the distance between successive equilibrium sites in the special case of self-diffusion of pure liquid water. f_{trans}, f_{rot}, f_{vib} are, respectively, the translational, rotational and vibrational partition functions of the normal state of the molecule or ion the activation of which determines the rate of the diffusion process

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[7] J. H. Wang, THIS JOURNAL, **73**, 510 (1951).

[8] B. B. Owen, private communication.

[9] J. H. Wang, THIS JOURNAL, **73**, 4181 (1951).

under consideration. $f^{\ddagger}_{\text{trans}}, f^{\ddagger}_{\text{rot}}, f^{\ddagger}_{\text{vib}}$ are the corresponding partition functions of the activated state of the ion or molecule, with the understanding that the translational degree of freedom of the activated state in the direction of diffusion has been removed. It is generally assumed that $(f^{\ddagger}_{\text{vib}}/f_{\text{vib}}) = 1$ for transport processes. If we consider the intermolecular translational motion as free translation in a "cage," $(f^{\ddagger}_{\text{trans}}/f_{\text{trans}})$ should be approximately equal to $h/[(2\pi mkT)^{1/2}V_f^{1/3}]$, where V_f is equal to the "free-volume" of each "cage." This consideration would suggest to us the definition of activation energy as $-R\text{d}[\ln(D/T^{1/2})]/\text{d}(1/T)$ according to equation (7). On the other hand if the intermolecular translational motion can be considered as harmonic oscillation with frequency ν such that $h\nu \ll kT$, then $(f^{\ddagger}_{\text{trans}}/f_{\text{trans}})$ becomes $(1 - e^{-h\nu/kT}) \cong h\nu/kT$ which suggests defining the activation energy as $-R\text{d}(\ln D)/\text{d}(1/T)$ according to equation (7). Since the actual intermolecular translational motion in liquid water is neither free translation nor a harmonic oscillation of frequency ν such that $h\nu \ll kT$, it appears that a correct definition of activation energy should be $-R\text{d}[\ln(DT^{\gamma})]/\text{d}(1/T)$ with $-1/2 < \gamma < 0$. Actually the value of $h\nu/kT$ for liquid water at 25° is about 0.97. Thus if we consider the intermolecular translational motion as harmonic oscillation we would get a value of γ that is very close to $-1/2$. However, because of the semi-crystalline structure of liquid water the potential barrier hindering the rotation of a water molecule in its normal state must be higher than that for the activated state. This would mean that the exponential index of T in f_{rot} may be higher than that in $f^{\ddagger}_{\text{rot}}$ which suggests that the unknown index γ in the above discussion may be higher than the value estimated above. Thus it is clear from these considerations that an exact determination of the activation energy for tracer-diffusion is still beyond our reach, but the definition $E = -R\text{d}(\ln D)/\text{d}(1/T)$ appears to be more plausible than the definition $E = -R\text{d}[\ln(D/T)]/\text{d}(1/T)$.

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The Use of Chlorine Trifluoride as a Fluorinating Agent

BY EUGENE G. ROCHOW AND IRA KUKIN

The commercial availability of chlorine trifluoride[1] made it desirable to investigate the possibility of using this compound instead of elementary fluorine in a number of reactions in which that element customarily is used. In the only published work concerning the use of chlorine trifluoride as a fluorinating agent[2] HgF_2, AgF_2, CuF_2, TiF_3, PtF_4 and PbF_3 (not PbF_4) were prepared by heating the free metal with chlorine trifluoride for three hours at 120°; CoF_3 is reported from Co_3O_4 and from $CoCl_2$ without details.[3]

Experimental

Preparation of Metal Fluorides.—Cobalt(III) fluoride, nickel(II) fluoride and silver(II) fluoride were prepared from cobalt(II) chloride, nickel(II) chloride and silver chloride, respectively. Fifty grams of the chloride first was heated in a porcelain dish for several hours at 250° to dry it, and then the anhydrous chloride was ground to pass a 30 mesh screen, and the powder was spread on a monel tray shaped to fit within a monel tube. The monel reaction tube (see Fig. 1) was similar in design to that used by Priest,[4] who designed it for the preparation of anhydrous metal fluorides by the action of free fluorine on metal chlorides.

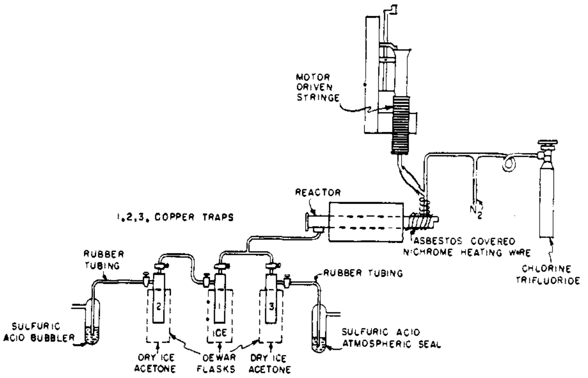

Fig. 1.—Complete apparatus assembly for preparation of fluorocarbons.

Nitrogen was passed through the reactor assembly of Fig. 1 and the furnace was heated to 250°. The flow of nitrogen was discontinued, the safety seal[4] was put in place, and the flow of chlorine trifluoride begun. During the fluorination, chlorine passed through the cold copper trap 3, and then bubbled out through the sulfuric acid outlet. The valve leading to copper trap 1 was kept closed during this fluorination cycle. The completion of the reaction was observed by the discontinuation of bubbles in the sulfuric acid outlet, since the trap was maintained at a temperature sufficiently low to condense the chlorine trifluoride (b.p. +11.3°) but not the chlorine (b.p. −33.7°).

The chlorine trifluoride then was purged from the system with dry nitrogen, and the reactor assembly was cooled. In the case of the cobalt(III) fluoride, the product was used directly for the fluorination of hydrocarbons. Its oxidizing value was determined by the oxidation of potassium iodide in caprylene[5] and was found to correspond to 90% CoF_3; the impurity was shown to be cobalt difluoride by a negative chloride test on the product. Prolonged fluorination with the chlorine trifluoride beyond the point of disappearance of chlorine at the outlet resulted in a product having an oxidizing value equal to that calculated for CoF_3.

It was found that the same reactor assembly could be used for fluorinating hydrocarbons. To do this, the valve leading to trap 3 was closed and the valves to traps 1 and 2 were opened; the hydrocarbons could then be introduced through a separate opening on the inlet tube of the reactor, by way of a metal valve. Several methods[6] for the introduction of the hydrocarbons were tried, but the use of a motor-driven syringe[7] proved most expedient. Alternation of the hydrocarbon feed and the chlorine trifluoride then allowed the same sample of cobalt fluoride to be used repeatedly without removing it.

The copper tubing and that portion of the reactor which extended in front of the electric furnace were wound with nichrome resistance wire to ensure volatilization of the hy-

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[1] Harshaw Chemical Company, Cleveland, Ohio.

[2] W. Huckel, *Nachr. Akad. Wiss. Gottingen Math. physik-Klasse*, 36 (1946).

[3] J. H. Simons, "Fluorine Chemistry," Academic Press, Inc., New York, N. Y., 1950.

[4] "Inorganic Syntheses," Vol. III, p. 171–183. See also Vol. VII-1 of the National Nuclear Energy Series, "Fluorine Technology," edited by Slesser and Schram (McGraw-Hill Book Co., Inc., New York, N. Y., 1951).

[5] Private communication from the Harshaw Chemical Company.

[6] R. D. Fowler and W. B. Burford: "Fluorocarbons," O.T.S. Report, Department of Commerce, Washington, D. C., 1947; *Ind. Eng. Chem.*, **39**, 292, 319, 329, 338, 350 (1947).

[7] This device is based in part on the automatic titrator designed by J. J. Lingane, *Anal. Chem.*, **20**, 285 (1948).