THE JOURNAL OF PHYSICAL CHEMISTRY

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VOLUME 62

APRIL 22, 1958

Number 4

ELECTRODE POTENTIALS IN FUSED SYSTEMS. IV. A THERMODYNAMIC AND KINETIC STUDY OF THE AgCl-NaCl SYSTEM¹

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The cell Ag/AgCl, NaCl/Cl₂ has been studied over the complete concentration range from pure AgCl to pure NaCl between 750 and 900°. For solutions very dilute in AgCl, silver reacts spontaneously with NaCl. The thermodynamic functions of the binary solution are given and compared with the corresponding bromide system. It is likely that galvanic cells do not yield thermodynamic data in the dilute region. The reaction $Ag + NaCl \rightarrow AgCl + Na$ has been studied in open and closed systems, and with 270-day Ag^{110m} tracer. Rates of reaction have been measured at several temperatures between 850 and 1080. The reaction is driven by the distillation of sodium.

Introduction

In paper II of this series² the cell Ag/AgCl, KCl/ Cl₂ was shown to behave reversibly from 0.05 mole fraction of AgCl up to the pure salt. It was shown that the free energy of dilution of AgCl by KCl is linear with concentration down to the lower value and then drops sharply toward minus infinity, *i.e.*, thermodynamic functions cannot be obtained for systems which behave irreversibly.

In agreement with the results obtained by Hildebrand and Salstrom³ for the AgBr-KBr system, the ΔF of dilution in the AgCl-KCl system also deviates negatively from ideality. Since the sign of the deviation is determined by the dilution of silver ion by the alkali metal cation, the anion only affecting its magnitude, it seemed of interest to extend our work to the AgCl-NaCl system. For the corresponding AgBr-NaBr system Hildebrand and Salstrom already found a positive deviation.

Our concern here is primarily with solutions dilute in silver. The free energy of dilution of the Ag-Cl-KCl system exhibits an abrupt break to a more negative slope near 0.05 mole fraction AgCl. For

(1) This research was supported by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command under Contract AF 18(600)-960. Reproduction in whole or in part is permitted for any purpose of the United States Government. Presented at the 131st meeting of the American Chemical Society, Miami, Fla., April 7-14, 1957.

(2) K. H. Stern, THIS JOURNAL, 60, 679 (1956).

(3) (a) E. J. Salstrom and J. H. Hildebrand, J. Am. Chem. Soc., 52, 4650 (1930);
(b) E. J. Salstrom, *ibid.*, 53, 1794 (1931);
(c) 53, 3385 (1931);
(d) 54, 4252 (1932);
(e) J. H. Hildebrand and E. J. Salstrom, *ibid.*, 54, 4257 (1932).

solutions more dilute than this, silver was found to react spontaneously with KCl to form AgCl and metallic potassium. If the same phenomenon should occur in the AgCl-NaCl system it would lead to a reversal of the slope of the free energy function-mole fraction plot. As our results show this is the case. Consequently, we also examined the kinetics of the reaction between silver and Na-Cl. To our knowledge the kinetics of reactions between metals and molten salts have not previously been reported though of course many such reactions are known and have been used for preparative purposes. This field is also of interest in con-nection with high temperature corrosion.⁴ The mechanism of many of these reactions is complex, however, and it is difficult even to isolate and identify the products. The reaction reported here is simple and may, on the basis of previous evidence,² be hypothesized as $Ag + NaCl \rightarrow AgCl + Na$.

The reaction was studied both in open and "closed" systems, using conventional gravimetric methods of analysis, and in an open system by a radiochemical method. "Closed" means in sealed Vycor capsules.

Experimental Part

Galvanic Cell.—The measurements on the galvanic cell Ag/AgCl, NaCl/Cl₂ were made by the same procedure that was used previously on the cell Ag/AgCl, KCl/Cl₂. The sodium chloride was of C.P. grade.

sodium chloride was of C.P. grade. Open System Kinetics.—A 25 \times 200 mm. Vycor test-tube was preheated to the desired temperature in a well insulated

(4) Cf. D. M. Mathews and R. F. Kruh, Ind. Eng. Chem., 49, 55 (1957).

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furnace, approximately 40 g. of NaCl added, the system again brought to temperature equilibrium and from 6 to 8 g. of silver added, the metal being variously in the form of sheet, buttons, or wire, uniformly of 99.99% purity (on the initial addition of silver to the melt, flashes of light were emitted, evidence of the initially rapid evolution of sodium vapor). In all the runs the metal was submerged well below the surface of the melt to prevent contact with atmospheric O_2 . The melt was constantly stirred by a hollow, motor-driven 9 mm. Vycor tube to minimize con-centration gradients. Stirring speed was approximately 250 r.p.m. Samples were withdrawn periodically with a Vycor tube for analysis. Temperature fluctuations were hold to 15° held to $\pm 5^{\circ}$. Since the reaction is very slow and relatively temperature insensitive these are probably rather unimporalumel thermocouple placed in a nickel protection tube. The hot junction was kept near the bottom of the melt. The furnace was well insulated and temperature gradients at the reaction site were negligible.

Closed System Kinetics.-15.00 g. of NaCl and 3.00 g. of Ag were weighed into a Vycor capsule made from 15 mm. tubing and sealed in under vacuum ($\sim 10^{-3}$ mm.). In each run from five to ten such capsules were placed in a furnace preheated to the desired temperature. At intervals they were withdrawn for analysis. Because of the expansion of alkali halides on solidification the vials usually cracked on cooling. The large pieces of glass on the outside of the vial were removed. The layers of glass next to the melt were too firmly attached to it to allow simple removal. This layer contained crystalline SiO_2 as well as metallic Si, produced through the reduction of SiO₂ by sodium vapor formed in the reaction $Ag + NaCl \rightarrow AgCl + Na$. (The reduction of SiO₂ by the alkali metals, according to

the equation $SiO_2 + 4Na \rightarrow 2Na_2O + Si$, is a standard method for the preparation of metallic silicon. That the reaction goes under the conditions of the above experiment was verified by scaling ~ 0.1 g of Na into a Vycor capsule under vacuum. After 24 hours at 800° the entire inside of the capsule was coated with a layer of black graphitic Si.) The melt was crushed, the large unreacted pieces of silver

removed and weighed, the melt was weighed, dissolved in NH4OH and the filtrate analyzed gravimetrically for silver by the sulfide method. The remaining solid containing Si, SiO₂ and tiny bits of metallic Ag was treated with HNO dissolve the silver. In this way a material balance could be run for silver. In most cases agreement was very good.

Silver concentration in both open and closed systems was calculated on the basis of (NaCl + AgCl) weight only. Vacuum Experiment.—To determine whether small quan-

tities of H_2O or O_2 were responsible for the reaction several grams of NaCl was heated slowly to about 850° in an apparatus similar to the one described under "Open System" except that the test-tube was enclosed in a vacuum system.

that the test-tube was enclosed in a vacuum system. The salt was dehydrated by heating under continuous pumping, silver added, and the pumping continued for 36 hours. Analysis of the cooled melt showed the presence of AgCl. **Radiochemical Method**.—Since the gravimetric analysis for silver is not very satisfactory for small amounts and since the initial course of the reaction is of interest, an "open system" run was made using 270 day Ag^{110m} as a tracer. Seven g. of the silver described above and 1 g. of Reagent Grade AgCl (used as standard) were irradiated 30 days in Grade AgCl (used as standard) were irradiated 30 days in the X-10 reactor at Oak Ridge at a flux of about 5×10^{11} neutrons/cm.²-sec. to produce 270 day Ag^{110m}.

The samples were counted by the integral-bias method on a scintillation spectrometer fitted with a 1.5×1 inch NaI-(TI) crystal, the discrimination level being set so that only γ -rays above 360 kev. were counted. In this way, the corrections for self-absorption and self-scattering in the source rections for self-absorption and self-scattering in the source (100 mg./cm.² on the average) were made negligible. Moreover, counting was carried out at two levels of discrimination in order to confirm that such corrections actually are negligible under these conditions. Background inside of a 4-inch thick lead shield was about 50 c./m. Duplicate samples were prepared and counted (twice each) to assure reproducibility, for at least 5 minutes. In all cases, the accuracy and reproducibility checked to within $\pm 2\%$, when counting was done on the same day to avoid correction for counting was done on the same day to avoid correction for radioactive decay and to minimize variations in electric gain of the scintillation counter. In order to calibrate the specific activity (counts/min. per mg.) of the samples in terms of mole-fraction of silver present, samples of the irradiated

AgCl were weighed and counted along with the samples

AgCl were weighed and counted along with the samples from the kinetic run. This calibration was evaluated to be $1.3 \times 10^{\circ}$ counts/min. per mg. = 1 mole Ag. This silver (specific activity ~ 2 × 10⁴ dis./sec. per mg.) was then used in a kinetic run at 857° as described under "open system" above. Samples of the melt were with-drawn at intervals for analysis. Since less than 50 mg. was sufficient for the detection of activity, many more samples (25 in all) could be taken than was possible by the conventional method. Moreover, since the method is very sensitive, kinetics for very short times could be obtained. Thus the first sample, taken 2 minutes after immersion of the silver in the melt, showed an activity of three times background, whereas the gravimetric technique restricted analysis to samples taken after 25 hours.

Results

The Cell Ag/AgCl, NaCl/Cl₂.—The temperature variation of the cell Ag/AgCl, NaCl/Cl₂ for various mole fractions of AgCl is shown in Table I. The mole fraction of AgCl is defined as

$$N_{\rm AgC1} = \frac{n_{\rm AgC1}}{n_{\rm AgC1} + n_{\rm NaC1}}$$

and the n's represent the number of moles of the component in question.

TABLE I

ELECTRODE POTENTIALS OF THE CELL

	Ag/Ag	Cl, NaCl/Cl ₂	•
NAgC	t(°C.)	E(v.)	$\mathrm{d}E/\mathrm{d}T imes10$
0.5260	741	0.8693	-1.88
	788	.8603	
	806	.8572	
	856	.8483	
	896	.8399	
.3331	766	.8947	-1.40
	812	.8867	
	871	.8779	
	918	.8736	
.2530	812	.9101	-1.49
	839	.9068	
	911	.8955	
	949	.8889	
. 1233	817	.9780	-0.648
	865	.9752	
	913	.9718	
.0891	813	1.0246	+0.308
	866	1.0329	
	926	1.0280	
.0775	844	1.0485	0,459
	895	1.0514	
	938	1.0530	

Several sets of data are now available for the cell $Ag/AgCl/Cl_2$. Because the potential of this cell, E^0 , is involved in all subsequent calculations a comparison is of interest. The earliest reliable measurement was made by Salstrom,⁵ who worked in the temperature range 460-600°. The results recently reported by the author² are within 2 mv. of Salstrom's data. While the current work was in progress I learned of similar work being done by a group at the Oak Ridge National Laboratory.⁶ Their measurements were carried to 800°. They are in substantial agreement with the studies cited above and show that dE/dt is linear over the

(5) E. J. Salstrom, J. Am. Chem. Soc., 55, 2426 (1933).

(6) M. B. Panish, R. F. Newton, W. R. Grimes, F. F. Blankenship; Dr. Panish has very kindly sent me the data in advance of publication.

entire range of temperature. E^0 values also have been computed from heat capacity data.⁷ While the agreement is close between these and the experimental values at the lower temperatures, the slope is sufficiently less so that the computed E^0 is about 20 mv. higher at 900° than the straight-line extrapolations of the experimental data. The experimental values probably are more reliable.

The curves, linear over the temperature range studied, are qualitatively similar to those for the AgCl-KCl system. One difference, however, is noticeable. For solutions below 0.1 N_{AgCl} the sign of dE/dT becomes positive. Since this quantity corresponds to the entropy of formation of AgCl in a medium of the indicated composition, it follows that the entropy term is favorable to the formation of AgCl in dilute NaCl, but not in KCl.

Open System Kinetics.—The dependence of silver concentrations on time for four temperatures is shown in Fig. 1. No correction has been made for the change of NaCl/Ag ratio resulting from the withdrawal of sample. The data for the radiochemical measurement are plotted in Fig. 2. Since the samples required for analysis were less than 50 mg., the NaCl/Ag ratio remained nearly constant during the entire run. This difference accounts for the divergence of the two 860° runs. The agreement with the data resulting from chemical analysis is quite good for the first 300 hours. The problem of determining the order of the reaction is quite difficult and will be treated in the Discussion. Several conclusions may be drawn.

1. Silver at concentrations near 10^{-5} mole fraction is found in the melt after only two minutes. This may be atomic or ionic silver. The radio-chemical method does not distinguish.

2. Over the range of time and concentration for which both chemical and radiochemical methods were used the concentration of silver found by both methods is nearly the same. Thus, at least after 20 hours, the silver in the melt is predominantly ionic.

3. The rate of reaction clearly increases with temperature. Closed System Kinetics.—The kinetic data for

Closed System Kinetics.—The kinetic data for the closed system runs are shown in Fig. 3. This set of runs was made to see whether (1) the presence of oxygen is necessary for the reaction to occur, and (2) preventing the distillation of sodium from the system prevents the reaction from occurring. This had been postulated previously.^{2,8}

The answer to question (1) is clearly negative, as is shown also by the experiment done under vacuum. The experiment does not provide a completely unambiguous answer to question (2), but is good evidence for the hypothesis. The reaction rate is definitely less in the sealed capsules than in the open tubes but the reaction of sodium with the SiO_2 of the container walls means that the system is not really closed in the thermodynamic sense. However, the reaction of SiO_2 is good evidence that the reaction is driven by the distillation of sodium. The distillation of sodium into the walls of the

(7) W. H. Hamer, M. S. Malmberg and B. Rubin, J. Electrochem. Soc., 103, 8 (1956).

(8) K. H. Stern, THIS JOURNAL, 60, 1443 (1956).





Fig. 2.—Change of NaCl concentration from radiochemical data in reaction NaCl + Ag^{110m} \rightarrow Ag^{110m} Cl + Na: upper curve shows the initial rate, lower curve the first 300 hours; $t = 857^{\circ}$.

sealed capsules would be slower than its distillation into the open atmosphere. It follows that the reaction would not go in a closed container of an inert material, but such a substance is difficult to



Fig. 3.—Kinetic data for the reaction Ag + NaCl \rightarrow AgCl + Na: closed system.



Fig. 4.—Thermodynamic difference function (excess free energy) $\Delta \bar{F}_1 - \Delta \bar{F}_1^{1} = RT \ln \gamma_1$, for some silver halidealkali halide systems: AgBr-NaBr, AgBr-KBr at 600°; AgCl-NaCl, AgCl-KCl at 800°; for references see text.



Fig. 5.—Excess free energy $(\Delta F^{\rm E} = RT \ln \gamma_1)$ for the AgCl-NaCl system at 900°.

find. Indeed, after about 100 hours capsules in the 1033° run evidently became permeable to salt after some time since white fumes could be seen coming through the closed capsules.

Discussion

Galvanic Cells.—In their study of the AgBralkali bromide systems Hildebrand and Salstrom³ found that the excess partial molal free energy of AgBr could be represented by an equation of the type $(\vec{F}_1 - \vec{F}_1) = BN_2^2$ where $\vec{F}_1 = RT \ln a_1$, $\vec{F}_1^i = RT \ln N_1$ and hence $(\vec{F}_1 - \vec{F}_1) = RT \ln \gamma_1$; subscripts 1 and 2 refer to silver bromide and alkali bromide, respectively. This was true, at least, for the solutions rich in AgBr. In Fig. 4 we have plotted $(\bar{F}_1 - \bar{F}_1)$ vs. N_2^2 , where N_2 is the mole fraction of alkali halide, for our data on the AgCl-KCl and AgCl-NaCl systems as well as these functions for the corresponding bromide systems. The data for the bromide systems are given for 650°, for the chloride systems at 900°. However, the entropy is so small as to make the difference negligible. This had been shown by Hildebrand and Salstrom for the bromide systems and also was true for our data; plots of the above functions for several temperatures give virtually the same curve.

From the four systems it seems reasonable to conclude that the anion has virtually no influence on the energies involved in diluting silver ions with alkali metal ions. Over the concentration range studied by Hildebrand and Salstrom our data are also nearly linear, but the deviation from linearity becomes extreme, particularly for the AgCl-NaCl system, on the alkali halide rich side. Parenthetically, our data on the AgCl rich side are also well represented by a first-power concentration dependence, as shown in Fig. 5. Clearly, the choice of E^0 makes a considerable quantitative, but virtually no qualitative, difference. The agreement between our data and those of Panish, *et al.*, is quite good on the silver rich side when the same E^0 is used.

(Since E^0 has now been measured by three independent investigators^{2,5,6} whose data agree to within 2 mv. over a large temperature range it would seem that the calculated values of Hamer, *et al.*,⁷ may be in error.)

The most striking disagreement with these workers occurs on the NaCl side where our data show a reversal of slope, quite analogous to the abrupt break for the AgCl-KCl system. The slight differences in the experimental arrangement reveal no cause for the discrepancy.

Our data are, however, consistent with the hypothesis that the data below approximately 10 or 12 mole % silver do not represent equilibrium values. For example, in some experiments in which silver was immersed in molten NaCl for several weeks the final composition of the melt was in this range. Since the reaction is very slow it would be possible to measure steady potentials (within a few tenths millivolt) over a period of an hour or two even though the reaction actually was proceeding. It is highly suggestive that the potentials of galvanic cells in which the silver concentration was less than 5 mole % did decrease perceptibly during the time of measurement.

Anticipating the results of our kinetic study in which we found the rate of AgCl buildup to be 7×10^{-5} mole fraction/hr. (at 860°) we get a change of 1 mv./hr. for the galvanic cells, which is in agreement with our observations, and with those reported previously² for the cell Ag/KCl/Cl₂.

The above results imply that thermodynamic data on silver halide-alkali halide solutions cannot be obtained from measurements on galvanic cells containing silver electrodes for solutions very dilute in silver ion, because silver reacts spontaneously with alkali halides. Thus, even though steady potentials may be measured over an hour or two, they may not represent true equilibrium values.

Of course, thermodynamic data on such solutions may be obtained from methods not involving the presence of metallic silver, *i.e.*, the solutions by themselves are most likely perfectly stable in the absence of the metal except for changes in composition resulting from the preferential vaporization of one component.

Kinetics.—We review first the evidence for our contention that the reaction between silver and sodium chloride is $Ag + NaCl \rightarrow AgCl + Na$ and that this is a driven reaction.

Consider the equilibrium properties of the system. Using the published E^0 values⁷ for AgCl and NaCl we calculate, for 850°, for the reaction Ag + NaCl \rightarrow AgCl + Na, $E^0 = -2.377$ v., $\Delta F^0 = 54.8$ kcal., $\Delta S^0 = -18.4$ e.u., $\Delta H^0 = 34.6$ kcal. The standard states are the pure substances for Ag, AgCl, and NaCl, and Na vapor at 1 atmosphere pressure. The equilibrium constant $K = 1.91 \times 10^{-11}$. If we let the activity equal the mole fraction we have, in the system at equilibrium

$$K = 1.91 \times 10^{-11} = \frac{P_{\text{Na}} N_{\text{AgC1}}}{N_{\text{Ag}} N_{\text{NaC1}}} = \frac{P_{\text{Na}} N_{\text{AgC1}}}{N_{\text{NaC1}}}$$

if the activity of pure silver is unity. Thus, in a closed system in which silver, sodium vapor at 1 atmosphere and NaCl are at equilibrium the concentration of AgCl should be 1.9×10^{-11} , below the limit of detection.

The reverse reaction goes rapidly to completion. This was verified by dropping a piece of sodium into AgCl just above its melting point (480°). The quenched melt contained silver metal.

Unfortunately, the situation in the real system is far more complicated. In addition to the changes in the AgCl/NaCl ratio with time caused by the reaction we must consider the state of the liberated sodium. If the metal and melt were immiscible one might speak of sodium vapor pressure above the melt with some precision. However, at the temperatures of these experiments the solubility of sodium in sodium chloride is considerable,¹⁰ varying from 5 mole % at 850° to 25 mole % at 950° and rising to a consolute temperature near 1060°. Thus it might be more apt to speak of the reaction being driven by the distillation of sodium, not outside the system, but simply into the melt. That sodium does appear in the melt is shown by the blue color of the reaction melts, characteristic of dissolved sodium. Similarly, silver is somewhat solu-

(10) M. A. Bredig, J. W. Johnson and W. T. Smith, J. Am. Chem. Soc., 77, 309 (1955).



Fig. 6.—Test of first-order kinetics for reaction $Ag + NaCl \rightarrow AgCl + Na$; data of Fig. 1.

ble in AgCl,¹¹ 0.06 mole % at 700°. Nothing is known of the solubility of silver in NaCl (as atomic silver). The occurrence of mass-transfer on silver electrodes immersed in NaCl suggests, however, that some solubility exists since otherwise the movement of silver from the hotter to the cooler portions of the electrode would be difficult to explain. It may be that the solution of silver is the initial step in the reaction. Since experimentally we find silver concentrations greater than 0.05 at 860° it is clear that when the solubility of sodium in NaCl is exceeded the metal must distil from the system. Some semi-quantitative experiments in which silver was added to NaCl over a period of two months indicate strongly that the reaction could be driven to completion if enough silver were added.

We next consider the order of the reaction. The rate law usually can be determined from a knowledge of reactant or product concentration changes with time. For a zero-order reaction the NaCl concentration is $N_2 = -kt$, whereas for a first-order reaction $\ln N_2 = -kN_2$. Now in the reaction between silver and sodium chloride the mole fraction of the salt, N_2 , is between 0.95 and unity. For numbers in this range the number itself and its logarithm are virtually identical. Thus, a priori, the data do not distinguish between zero and first-order reactions.

A plot of the $\log N_2 vs.$ time of the data in Fig. 1 is shown in Fig. 6. A plot of $N_2 vs.$ time appears virtually identical. All the curves show an initial slow-rate section and a subsequently more rapid one. The initial period decreases with increasing temperature. Only the 1080° curve is linear over the steep section. Rate constants for this section

(11) J. D. Corbett and S. von Winbush, ibid., 77, 3964 (1955).

calculated from zero and first-order rate laws are virtually identical, 1.67×10^{-5} mole fraction hr.⁻¹ and 1.70×10^{5} hr.⁻¹, respectively. The break toward a lower rate in the 890° curve may represent an approach to equilibrium, *i.e.*, the effect of the reverse reaction Na + AgCl \rightarrow NaCl + Ag.

Since both zero- and first-order treatment yield nearly the same rate constants the same activational energies will apply in either case. The 890 and 970° data do not give very straight lines. However, from the straight-line portion of the 1080° and the 200-300 hour section of the 860° run (k = 8.9×10^{-5} hr.⁻¹) we obtain as an estimate for the activational enthalpy $\Delta H^* = 9.7$ kcal. The entropy of activation, ΔS^* , can be calculated from the theory of absolute reaction rates

$$k_{\rm T} = \frac{kT}{h} e^{\Delta S^*/R_e - \Delta H^*/RT}$$
(1)

Since $k_{\rm T}$ is in hr.⁻¹, kT/h is in molecules⁻¹ hr.⁻¹ = 8.35 × 10¹⁶. Solving the equation we get $\Delta S^* = -99.0$ e.u. The free energy of activation is

$$\Delta F^* = \Delta H^* - T \Delta S^* \tag{2}$$

At 861° we get $\Delta F^* = 109$ kcal. The present data are not sufficient to establish a mechanism for the reaction. Broadly it may be described as an electron exchange reaction between atoms and ions characterized by a large negative entropy of activation; this appears to be primarily responsible for the slow rate of reaction, since ΔH^* is relatively small. For reactions of this type in aqueous solution these characteristics have been associated^{12,13} with a very low electronic transmission coefficient $k_e = e^{\Delta S^*/R}$. Unfortunately, the equations have been derived only for aqueous solutions, particu-

(12) R. J. Marcus, B. J. Zwolinski and H. Eyring, This Journal, 58, 432 (1954).

(13) B. J. Zwolinski, R. J. Marcus and H. Eyring, Chem. Revs., 55, 157 (1955).

larly exchange reactions in which the chemical species are indistinguishable, *i.e.*, $\Delta F^0 = 0$. Nevertheless, there is a certain correspondence between the reactions treated by Marcus, Zwolinski and Eyring and the present one.

If it is assumed that $\Delta S^* = R \ln k_e$ and that the reaction is homogeneous (the initial step being the solution of silver in NaCl as atoms) then the tunnel distance r_{ab} at which electron-exchange occurs can be calculated from the expression

$$\ln k_{\rm e} = -\frac{8\pi}{3h} r_{\rm ab} \left[2me^2 \left(\frac{Z^*}{2r_0} - \frac{f(n)}{Dr_{\rm ab}} \right) \right]^{1/2} \quad (3)$$

where m = mass of the electron, $Z^* = \text{the positive}$ charge = 1, $r_0 = n^{*2}a_0$, $n^* = \text{effective quantum}$ number for Na = 1.63, $a_0 = 0.528 \times 10^{-8}$ cm., f(n) is a function of charge = 1 for the charge transfer between an atom and a univalent ion, D = dielectric constant. If we let D = 3, customary for fused salts, $r_{ab} = 35$ Å., which seems unreasonably large since it is difficult to visualize a mechanism by which an electron can be transferred over such a large distance. However, electron transfer during atom-ion collision in the melt cannot be ruled out.

Alternatively, insufficient evidence is available to establish a heterogeneous mechanism which would have as its initial step the adsorption of sodium ions on the metallic silver surface.

Certainly more work on this reaction, including the effect of surface area and stirring speed on rate, as well as studies on other reactions of this type, is needed.

Acknowledgment.—I wish to thank Mr. Thomas Wilson, a summer research assistant from El Dorado High School, for doing the "closed system" kinetics; Dr. R. W. Fink for his help and advice with the radiochemical experiment, and for the use of his counting equipment; and Mr. K. Okada for the actual counting.

ION-EXCHANGE SEPARATION OF BERYLLIUM BY ELUTION WITH SALICYLATE ANALOGS¹

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Received June 6, 1957

Rapid quantitative separations of trace quantities of Be from macro-concentrations of salts including those of Cu, U and Ca were devised. The method makes use of the fact that Be forms a relatively strong complex with salicylate analogs in the region pH 3-4.5 whereas most cations of the alkaline earths do not react significantly with salicylates, and cations such as Cu⁺⁺ and UO₂⁺⁺ react weakly or not at all in the same pH region. The separation of Be from foreign cations is made by means of a cation-exchange resin. Be is eluted selectively with 0.02-0.10 *M* sulfosalicylic acid (SSA) at pH 3.5-4.5. Neither Cu⁺⁺, UO₂⁺⁺ nor Ca⁺⁺ are removed under these conditions. Uranylion is eluted by SSA at pH 4.5-4.7. The foreign cations can be removed subsequently by a variety of eluting agents such as HCl and H₂SO₄. At pH > 6 and in the presence of SSA Be is strongly absorbed by an anion-exchange resin. Evidence is given to show that in the acid regions Be forms an uncharged complex with SSA and a negatively charged complex in neutral and elkaline regions.

The sensitivity of analytical procedures for beryllium is severely limited by the presence of interfering substances.^{2a-c} This problem becomes

(1) Work performed under the auspices of the U.S. Atomic Energy Commission.

(2) (a) T. Y. Toribara and R. E. Sherman, Anal. Chem., 25, 1594
(1953); (b) J. R. Arnold and H. A. Al-Salih, Science, 121, 451 (1955);
(c) A. J. Cruikshank, G. Cowper and W. E. Grummitt, Can. J. Chem., 34, 214 (1956).

especially acute when it is necessary to isolate micro-quantities of Be from biological and geological materials. Usual methods of extraction and precipitation in such cases are not only laborious and time-consuming but often give low or erratic results. Since the discovery that the radioactive nuclides, Be⁷ and Be¹⁰, are produced in the atmosphere by cosmic rays,^{2b} it is especially worth-