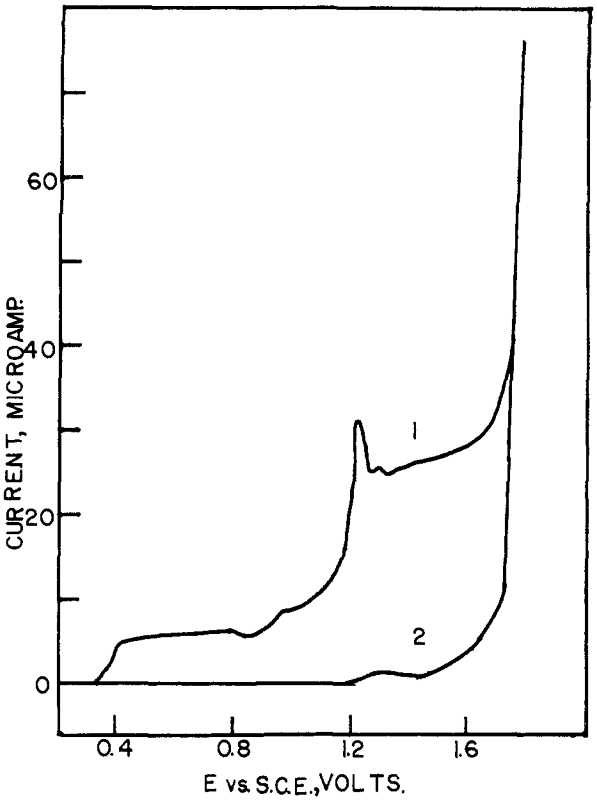

Fig. 6.—(1) Current-potential curve for 0.94 milliformal iodide ion in 1 *F* sulfuric acid with a gold microelectrode; (2) residual current.

that the current-potential curve show some current limited section corresponding to zero iodine concentration at the electrode surface. The current-density and rate of electrode potential change are quite different in chronopotentiometric and current-potential experiments, but it was not possible to explain the apparent discrepancy between the two experimental results by controlling these variables. It is probable that this difference between chronopotentiometric and polarization curve techniques is associated with the nature and rate of formation of the oxidized film on the electrode and with the film's reactivity. It is hoped that the continued study of this phenomenon will lead to a better understanding.

The current-potential curve in Fig. 6 for the gold microelectrode shows a sharp maximum at the potential where gold is oxidized, followed by a fairly well defined limiting current section prior to oxygen evolution. This much more definite indication of iodine oxidation at a gold electrode results from the significantly more oxidizing potentials at which water is oxidized on gold.

The second limiting current observed with the gold microelectrode is not six times as large as the first iodide limiting current, and it should not be if oxidation to iodate is occurring. Reaction between the iodate diffusing away from the electrode and the iodide diffusing toward the electrode will result in iodine being formed. This iodine will now diffuse both toward and away from the electrode since its concentration will be negligible both at the electrode surface and in the body of the solution. The effect of this reaction will be to decrease the current because of both the smaller diffusion coefficient of iodine and the diffusion of some of the iodine away from the electrode. Conversely, since iodine will have been accumulating at the electrode all during the time the iodide limiting current was observed, when oxidation of iodide above iodine commences there already will be some iodine at the electrode and in the solution near the electrode which will also be oxidized. This will tend to increase the limiting current observed for oxidation to iodate. The resultant of these opposing effects is not readily calculable but in view of their qualitative significance and direction of operation the observed ratio of 4.4 for the two limiting currents with the gold anode is compatible with oxidation to iodate.

Acknowledgment.—We are grateful to Dr. William Klemperer and Dr. C. N. Reilley for helpful discussions. Appreciation is expressed to the Mallinckrodt Chemical Works for partial financial support and to the National Heart Institute for a fellowship held by one of us (F.C.A.).

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

Kinetics of the Manganate–Permanganate Exchange Reaction[1]

BY JOHN C. SHEPPARD AND ARTHUR C. WAHL

RECEIVED OCTOBER 15, 1956

In 0.16*f* NaOH the isotopic exchange reaction between MnO_4^{--} and MnO_4^- obeys over a wide range of reactant concentrations the law rate = $k(MnO_4^{--})(MnO_4^-)$. At 0° the value of k is 710 ± 30 M^{-1} sec.$^{-1}$. The experimental activation energy is 10.5 ± 1.0 kcal. The rate increases with increasing electrolyte concentration. The rate depends on the nature of the cations present but is affected very little by the nature of the anions. At constant electrolyte concentration $k_{CsOH} > k_{KOH} > k_{NaOH} = k_{LiOH}$.

In a previous communication[2] we reported the successful rate measurement of the rapid isotopic exchange reaction between manganate and permanganate ions. In this paper we report the results of additional kinetic studies.

Experimental

Chemicals.—Mallinckrodt "analytical reagent" grade chemicals were used without further purification, except for the following. NaOH, Baker and Adamson "reagent special" was used. KOH, Mallinckrodt "analytical re-

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[1] This work was supported by the National Science Foundation. The paper was abstracted from the Ph.D. thesis of John C. Sheppard, Washington University, 1955.

[2] J. C. Sheppard and A. C. Wahl, THIS JOURNAL, **75**, 5133 (1953).

agent" was recrystallized. LiOH, Fisher "purified" $LiOH \cdot H_2O$ was used. CsOH, excess silver oxide was added to a solution of cesium iodide, and the resulting suspension was filtered. $KReO_4$ was obtained from the Fairmont Chemical Co. Tetraphenylarsonium chloride was obtained from the Hach Chemical Co. $Na_3Fe(CN)_6 \cdot H_2O$, Fisher "purified" reagent, was precipitated twice from 95% ethanol. $Co(NH_3)_6Cl_3$, the preparation method of Bjerrum and McReynolds[3] was followed. $Na_3Co(CN)_6$, Bigelow's[4] method of preparation of $K_3Co(CN)_6$, was modified. Precipitation of the very soluble sodium salt was accomplished by addition of 95% ethanol. The precipitation was repeated four times.

Manganese Tracer.—The 310-day Mn^{54} tracer in the form of manganous ion was obtained from the Oak Ridge National Laboratory on allocation from the U. S. Atomic Energy Commission. A sample followed for 930 days decayed with a half-life of 320 days. Further proof of the radiochemical purity of the tracer was the equality of the manganate and permanganate "infinite-time" specific activities, determined periodically during the course of this work.

Tagged manganate ion was prepared by fusion of tagged manganese dioxide with sodium or potassium hydroxide. The cooled melt was dissolved in sufficient cold water to give a 3 M OH^- solution, which, after removal of unreacted manganese dioxide by centrifugation, was stored at 0°. The unreacted manganese dioxide was reused, or new tagged manganese dioxide was made from the manganous ion tracer by oxidation with excess potassium permanganate, the excess being reduced to manganese dioxide by hydrogen peroxide.

Separation Method.—Of the various separation methods investigated[2] the most satisfactory was the coprecipitation of permanganate ion with tetraphenylarsonium perrhenate. Tetraphenylarsonium permanganate is slightly soluble, but at the low concentrations used ($\sim 10^{-4}$ M) several seconds were required for the precipitate to form. When perrhenate ion was present at 4×10^{-4} M the mixed precipitate formed immediately. The apparent "zero-time" exchange was reproducible for any given set of conditions, and for various conditions ranged from 10 to 50%.

Special Apparatus.—A schematic diagram of the apparatus used in most of the experiments is shown in Fig. 1. The reactant solutions in the two reservoirs of the mixer were forced by compressed air through the three-way stopcock, in which they were mixed, into the reaction vessel, a 40-ml. centrifuge tube. A known time later the quenching solution of tetraphenylarsonium chloride was forced by compressed air into the reaction vessel. The air pressure over the reactant solutions and over the quenching solution was controlled by solenoid valves so that the time interval between the activation of the mixer and the activation of the quencher could be accurately timed electrically.

The reservoirs were 20-ml. vessels having ground-joint openings through which solutions were introduced. The openings were closed with plugs having 0.5-mm. capillaries to accommodate the small air leakage past the solenoid valves. The three-way stopcock and connecting capillaries had 2-mm. bores.

A single switch activated an electric timer, which was accurate to ±0.01 second, and opened the first solenoid valve for one second during which the reactant solutions were forced to mix and flow into the reaction vessel. A second switch stopped the timer and opened the second solenoid valve to force over the quenching solution. The delay circuit controlling the first solenoid valve was a modification of one described by Taylor and Reid.[5]

The stopcock was adjusted until the delivery rates from the two reactant vessels were equal within 2%. Each stopcock setting was tested by mixing standard acid and base and titrating of the one in excess. The efficiency of the adjusted mixer was tested by mixing 0.129 f NaOH containing phenolphthalein with an equal volume of 0.132 f HCl. The mixed solution entering the reaction vessel was colorless so the mixing at this point was greater than 95% complete. A motor-driven glass propeller stirrer completed the mixing.

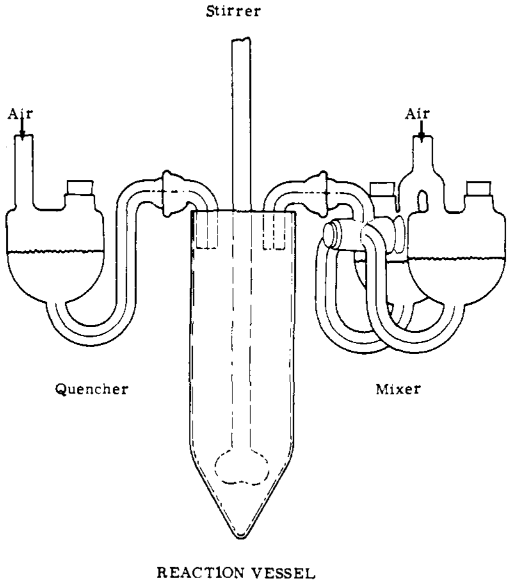

Fig. 1.—Schematic diagram of exchange apparatus.

The apparatus described above was useful for measurements of half-times greater than one second. For shorter half-times a flow apparatus which is described by Gordon[6] was used.

Procedure.—The mixing apparatus and the reactant solutions were placed in a water-bath of the desired temperature. After thermal equilibrium had been attained, equal volumes (4.00 or 5.00 ml.) of the reactant solutions were placed in the mixer reservoirs, and 3 ml. of 0.1 f $(C_6H_5)_4AsCl$ solution was placed in the quencher reservoir. After seven minutes for re-attainment of thermal equilibrium, air pressure of 12 p.s.i. was applied first to the reactant solutions to start the reaction and then to the quenching solution to stop it as described in the previous section. The capillary tips, which were connected to the mixer and quencher through semi-ball joints, and the stirrer were then removed from the reaction vessel, and the precipitate was separated from the supernatant solution by centrifugation and washed with a dilute solution of tetraphenylarsonium chloride. The supernatant solution, which contained the MnO_4^{--}, and the wash were discarded. The specific activity of the manganese in the precipitate was determined as described in the next section.

In each run the above procedure was repeated 9 to 11 times, the reaction time being varied. Usually the first and last were infinite-time points (*i.e.*, the exchange was allowed to run a few minutes to completion). The reactant concentrations were determined spectrophotometrically by analysis of each reactant solution. Permanganate ion was determined directly; the manganate ion was determined as MnO_4^- after reduction and oxidation as described in the next section.

Because of the instability of MnO_4^- in alkaline solution, all of the alkali was placed in the MnO_4^{--} solution. A check showed that the rate was the same when the alkali was equally distributed between the two reactant solutions. Perrhenate ion and any added salts were in the MnO_4^- solution.

All of the apparatus except the delivery tube was thermostated to better than ±0.1°. Tests with a thermocouple in the reaction vessel showed that the temperature of the mixed reaction solution on entering the vessel had risen $<0.1°$.

Specific Activity.—The tetraphenylarsonium permanganate–perrhenate precipitate was dissolved by boiling in a 0.3 f HNO_3 solution containing a little sodium acid sulfite. Sodium perchlorate was then added to precipitate the tetraphenylarsonium ion, and the solution was filtered. The manganous ion in the filtrate was oxidized to permanganate

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[3] J. Bjerrum and J. P. McReynolds, "Inorganic Syntheses," Vol. II, W. C. Fernelius, editor, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 217.

[4] J. H. Bigelow, ref. 3, p. 225.

[5] J. K. Taylor and J. G. Reid, *Ind. Eng. Chem., Anal. Ed.*, **18**, 79 (1946).

[6] B. M. Gordon, Ph.D. thesis, Washington University, 1955.

ion by ammonium peroxydisulfate. Nydahl's[7] procedure was modified by allowing the oxidation to proceed at room temperature overnight after an initial warming to start the reaction. The optical density of the resulting solution was then determined at 5100 Å., where the molar extinction coefficient for permanganate ion is 1820. Three milliliters of the same solution was then diluted in a calibrated six-inch test-tube to a predetermined level and counted on a scintillation counter having a stilbene crystal. Manganese-54 emits a 0.835 Mev. γ-ray that was conveniently detected.

The fraction exchange was calculated by dividing the specific activity (counts per min./optical density) of a sample by the average of the specific activity values for the infinite-time samples. The data were plotted as illustrated in Fig. 2, and the half-time was read from the plot.

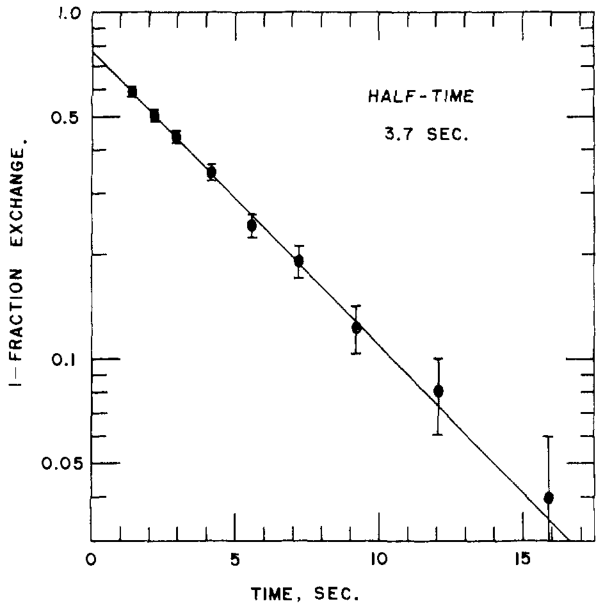

Fig. 2.—Typical exchange curve—conditions: 0.1°, 0.16 f NaOH, 0.08 f Na_2SO_4, $4 \times 10^{-4} f$ $KReO_4$, 0.40×10^{-4} M MnO_4^{--}, 0.96×10^{-4} M MnO_4^-. The errors shown correspond to ±0.02 in the fraction-exchange values.

Results

If the exchange reaction obeys the rate law

$$\text{Rate} = k(MnO_4^{--})(MnO_4^-) \qquad (1)$$

the rate constant k is related to the half-time $t_{1/2}$ by the expression[8]

$$k = \frac{\ln 2}{t_{1/2}[(MnO_4^{--}) + (MnO_4^-)]} \qquad (2)$$

This expression was used to calculate values of the rate constant from the measured half-times. As shown in Table I the values of k do not vary as the reactant concentrations are varied; thus equation 1 is valid.

The dependence of the rate on temperature is shown in Table II. The increase in rate as the temperature is changed from 0.1 to 21.9° corresponds to an activation energy of 10.5 ± 1.0 kcal. Rate constants calculated from this value are listed in the last column of Table II.

Tables III and IV show the effect on the rate of the electrolyte concentration.

TABLE I

RATE DEPENDENCE ON MnO_4^{--} AND MnO_4^- CONCENTRATIONS

(0.16 f NaOH, 0.1°)

(MnO_4^{--}), $M \times 10^4$	(MnO_4^-), $M \times 10^4$	$t_{1/2}$, sec.	k, M^{-1} sec.$^{-1}$
0.43	0.48	10.6	720
.41	0.48	11.2	700
.46	0.97	6.6	730
.45	1.46	5.3	680
.43	1.94	4.3	680
.42	2.43	3.2	760
.41	3.40	2.5	730
.10	0.97	9.2	700
.23	.95	9.0	650
.46	.97	6.6	730
1.01	.97	4.9	710
1.97	.97	3.1	760
3.30	33.7	0.25	750
19.5	18.8	0.26	700
2.90	38.1	0.25	680
		Av.	710 ± 30

TABLE II

RATE DEPENDENCE ON TEMPERATURE

(0.16 f NaOH)

Temp., °C.	(MnO_4^{--}) + (MnO_4^-), $M \times 10^4$	$t_{1/2}$, sec.	k, M^{-1} sec.$^{-1}$ Obsd.	Calcd.[a]
0.1	(Av. from Table I)		710	"710"
7.8	1.89	3.6	1000	1200
10.8	1.36	2.9	1800	1500
10.7	1.32	2.9	1800	
21.9	1.32	1.9	2800	3000
21.9	1.35	1.8	2900	
21.9	1.36	1.4	3600	
21.7	9.18	0.24	3100	

[a] Activation energy of 10.5 kcal. used; normalized at 0.1°.

TABLE III

RATE DEPENDENCE ON ELECTROLYTE CONCENTRATION

(0.1°)

Cation concn., M	k, M^{-1} sec.$^{-1}$ Li^+	Na^+	K^+	OH^- concn., M	Other anions	Ionic strength
0.08	..	605	610	0.08	....	0.08
.16	700	720	800	.16	....	.16
.32	..	920	1480	.32	....	.32
	..	990	..	.16	SO_4^{--}	.40
	..	880	..	.16	PO_4^{-3}	.48
	..	900	..	.16	$P_2O_7^{-4}$	.56
.57	1140	1140	2150	.57	....	.57
	..	1150	..	.16	Cl^-	.57
	..	1350	..	.16	SO_4^{--}	.77
	..	1310	..	.16	$Co(CN)_6^{-3}$	.98
.99	..	1700	..	.99	....	.99

TABLE IV

MISCELLANEOUS RATE DATA

(0.1°)

Medium	(MnO_4^{--}), $M \times 10^4$	(MnO_4^-), $M \times 10^4$	k, M^{-1} sec.$^{-1}$
0.08 f CsOH, 0.08 f NaOH	0.40	0.98	1730
0.16 f CsOH	.40	.98	2470
$10^{-3} f$ $Co(NH_3)_6Cl_3$, 0.16 f NaOH	.30	.98	1860
$10^{-3} f$ $Na_3Fe(CN)_6$, 0.16 f NaOH	.42	1.01	1180

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(7) F. Nydahl, *Anal. Chim. Acta*, **3**, 144 (1949).

(8) See, for example, O. E. Myers and R. J. Prestwood, "Radioactivity Applied to Chemistry," A. C. Wahl and N. A. Bonner, editors, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 11.

Discussion

In 0.16 *f* NaOH, the conditions under which the temperature was varied, the rate constant is given by the Arrhenius expression

$$k = (2 \times 10^{11})e^{-10500/RT},\ M^{-1}\ \text{sec.}^{-1}$$

and the calculated values of the entropy and free energy of activation[9] are $\Delta S^{\ddagger} = -9$ e.u., $\Delta F^{\ddagger} = 12.4$ kcal./mole.

It is of interest to compare the electron tunnelling hypothesis of Marcus, Zwolinski and Eyring[10] with these data. Since there is an uncertainty about the value of Z^*, the charge on the manganese atom in MnO_4^{--}, calculations were made for three different values, 6, the oxidation number, 3, the formal charge, and 1, the charge obtained from a molecular orbital treatment by Wolfsberg.[11] The results of the calculations are given in Table V, in which r_{ab} is the optimum distance of approach between the centers of the reactants, $\Delta F^{\ddagger}_{rep}$ is the electrostatic contribution to the free energy of activation, $\Delta F^{\ddagger}_{r}$ is the free energy of activation arising from reorganization of the coördination and hydration shells of the reactants, and κ_e is the probability of an electron penetrating the barrier. The corresponding values calculated[10] for the Fe^{++}–Fe^{+++} exchange are included for comparison.

TABLE V

COMPARISON OF ELECTRON TUNNELLING MODEL WITH EXPERIMENTAL DATA

(All energy values are in kcal./mole, 0°, D = 88.)

Reaction	Z^*	r_{ab}, Å.	$\Delta F^{\ddagger}_{rep}$	$\Delta F^{\ddagger}_{r}$	$-RT \ln \kappa_e$
MnO_4^{--}–MnO_4^-	6	2.6	2.9	6.6	2.9
	3	3.1	2.4	7.5	2.5
	1	4.0	1.9	8.7	1.8
Fe^{++}–Fe^{+++}	2	6.0	3.8	8.5	4.4

The calculated results are not very sensitive to the value of Z^*. The small values of r_{ab} are not consistent with the model, which assumes that the electron tunnels through the barrier when the reactants are separated by sufficient water that the macroscopic value for the dielectric constant is applicable. For ions the size of MnO_4^{--} and MnO_4^- this distance would have to be considerably larger than the calculated values of r_{ab}. Also $\Delta F^{\ddagger}_{r}$ is approximately the same for the MnO_4^{--}–MnO_4^- reaction as for the Fe^{++}–Fe^{+++} reaction. This is not reasonable because much less reorganization should be required for the MnO_4^{--}–MnO_4^- system in which the ions have the same structure[12] and being large are only loosely hydrated. *It is clear that the electron tunnelling hypothesis of Marcus, Zwolinski and Eyring*[10] *is not a reasonable model for* MnO_4^{--}–MnO_4^- *exchange.*

An examination of Table III shows that the effect on the rate of added "inert" electrolytes is due predominantly to the cations, the nature of the anions having little or no effect. Thus the rate is better correlated with the concentration of a specific cation than with the ionic strength, a conclusion in agreement with the findings of Olson and Simonson.[19]

It is to be noted that the various cations are not equally effective in increasing the rate, Cs^+ being more effective[20] than K^+, and K^+ being more effective than Na^+ or Li^+. This specific effect of cations could be due to incorporation of a cation into the activated complex, for example, to form a bridged activated complex such as $[MnO_4\text{–}K\text{–}MnO_4]^{-2}$, analogous to the anion bridge between cations for which evidence has been presented by Taube, Myers and Rich.[22,23]

It is also possible that the specific cation effect is due to the more general influence of the cation atmosphere on the activity coefficients of the reactants and activated complex. Calculations by Scatchard[24] have shown that cations of different charges should have grossly different effects on the rate of reaction between anions having charges of −1 and −2. The results of the calculations are quite sensitive to the value chosen for the distance of closest approach, so it seems reasonable that the alkali metal ions, having different hydrated radii, could affect activity coefficients and therefore rates differently.

The border line between the specific and nonspecific interactions is obviously fuzzy, and it is not possible from our data to choose between the above interpretations. Beringer and Gindler[25]

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[9] S. Glasstone, K. J. Laidler and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, pp. 417, 433.

[10] R. J. Marcus, B. J. Zwolinski and H. Eyring, *J. Phys. Chem.*, **58**, 432 (1954).

[11] M. Wolfsberg, Ph.D. Thesis, Washington University, 1951, p. 164.

[12] Wolfsberg and Helmholz[13] and Mooney[14] have shown that MnO_4^- is tetrahedral. The Mn–O distance in $KMnO_4$ is 1.59 Å.[14] Since MnO_4^{--} salts are isomorphous with SO_4^{--} salts, and SO_4^{--} is known to be tetrahedral,[15] MnO_4^{--} must also be tetrahedral. The crystal structure of MnO_4^{--} salt has not been determined, but Gordon[16] has determined the cell dimensions of K_2MnO_4. These data and the cell dimensions[17] of K_2SO_4 and K_2CrO_4 are summarized below.

	a_0, Å.	b_0, Å.	c_0, Å.
K_2SO_4	10.01	7.42	5.73
K_2CrO_4	10.40	7.61	5.92
K_2MnO_4	10.49	7.66	5.91

The S–O distance in SO_4^{--} is 1.51 Å.,[18] and the Cr–O distance in CrO_4^{--} is 1.60 Å.[17] Since K_2CrO_4 and K_2MnO_4 have nearly the same cell dimensions and belong to the same space group ($V_h{}^{16}$), the Mn–O distance must be close to the Cr–O distance, probably 1.61 or 1.62 Å. Thus the difference between Mn–O distances in MnO_4^{--} and MnO_4^- is well within the ~0.05 Å. zero-pont vibrational displacement estimated from the stretching frequencies and force constants for SO_4^{--} and ClO_4^-.[15]

[13] M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

[14] R. C. L. Mooney, *Phys. Rev.*, **37**, 1306 (1931).

[15] G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 167.

[16] B. M. Gordon, unpublished work done at Washington University.

[17] R. W. G. Wyckoff, "Crystal Structures," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1951, Chap. VIII, table, p. 47.

[18] A. C. Larson and L. Helmholz, *J. Chem. Phys.*, **22**, 2049 (1954).

[19] A. R. Olson and T. R. Simonson, *ibid.*, **17**, 1167 (1949).

[20] Since the cesium hydroxide was prepared by saturating cesium iodide with silver oxide, and silver oxide is appreciably soluble in alkaline solution,[21] it has been suggested by E. L. King that the large rate in cesium hydroxide might be due to catalysis by silver(I) through an equilibrium such as

$$AgO^- + MnO_4^{--} + H_2O = Ag + MnO_4^- + 2OH^-$$

We plan to check this possibility.

[21] H. L. Johnson, F. Cuta and A. B. Garrett, THIS JOURNAL, **55**, 2311 (1933).

[22] H. Taube, H. Myers and R. L. Rich, *ibid.*, **75**, 4119 (1953).

[23] H. Taube, *ibid.*, **77**, 4481 (1955).

[24] G. Scatchard, *Natl. Bur. Standards Circular*, **524**, 185 (1953).

[25] F. M. Beringer and E. M. Gindler, THIS JOURNAL, **77**, 3200 (1955).

in discussing kinetic effects of added "inert" electrolytes conclude that from kinetic data only the choice is difficult, if not impossible. The very effective catalysis by $Co(NH_3)_6^{+++}$ is analogous to the catalysis of the bromoacetate–thiosulfate reaction[26] by La^{+++} and is reasonable by either interpretation.

We believe the catalysis by $Fe(CN)_6^{---}$ involves the rapid reversible reaction[27]

$$MnO_4^- + Fe(CN)_6^{----} \underset{k_2}{\overset{k_1}{\rightleftarrows}} MnO_4^{--} + Fe(CN)_6^{---} \quad K' = \sim 200 \qquad (5)$$

The rate under the experimental conditions is given by

$$R = 1180(MnO_4^{--})(MnO_4^-) = 710(MnO_4^{--})(MnO_4^-) + k_2(MnO_4^{--})(Fe(CN)_6^{---})$$

$$k_2 = 470\,\frac{(MnO_4^-)}{(Fe(CN)_6^{---})} = 470\,\frac{(10^{-4})}{(10^{-3})} = 47$$

$$k_1 = K'k_2 = (\sim 200)(47) = \sim 10^4 M^{-1}\ \text{sec.}^{-1}$$

This value of k_1 is approximately the value we estimated from visual observations of the color changes that occur when MnO_4^- and $Fe(CN)_6^{----}$ are mixed in 0.1 *f* KOH at 5°.

Acknowledgment.—We wish to thank Professor E. L. King of the University of Wisconsin for reading the manuscript and making many valuable comments.

St. Louis, Missouri

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[26] V. K. La Mer and M. E. Kamner, This Journal, **57**, 2662 (1935).

[27] The value of the equilibrium constant was estimated from the formal potential[28] of the $Fe(CN)_6^{----}$–$Fe(CN)_6^{---}$ couple in 0.083 *f* Na_2SO_4 and the $E°$ value[29] of the MnO_4^{--}–MnO_4^- couple, both at 25°. No correction for temperature was made.

[28] I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, **39**, 945 (1935).

[29] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952, p. 239.

[Contribution from the Chemical Laboratory of the University of Kansas]

Activity Coefficients in Aqueous Zinc Chloride–Hydrochloric Acid Solutions, and their Application to Cation Exchange Data[1]

By Norman J. Meyer, William J. Argersinger, Jr., and Arthur W. Davidson

Received October 4, 1956

The equilibrium quotient for the zinc–hydrogen exchange on Dowex 50 in aqueous chloride solutions has been determined as a function of resin composition at constant total solution ionic strengths of 0.5 and 1.0 *m*. Approximate values of the solution activity coefficient ratios, obtained from electromotive force measurements on mixed hydrochloric acid–zinc chloride solutions and the application of Harned's rule, are used to compute the thermodynamic equilibrium constant for the exchange process and the activity coefficients of the resin components. The values obtained for the equilibrium constant are 10.2 at 0.5 *m* ionic strength and 11.7 at 1.0 *m* ionic strength.

Introduction

Equilibrium in the process of cation exchange on a synthetic resin such as Dowex 50 may be formulated in terms of a thermodynamic equilibrium constant which includes the activity coefficients of the components of the resin phase. The method of calculation of these quantities which has been developed in several previous papers from this Laboratory[2–5] has been applied to a number of exchange systems involving two univalent cations[2–9] and to a smaller number of exchange systems involving either two bivalent ions or one bivalent ion and one univalent ion.[10] At least one earlier study[11] was made of systems involving the exchange of bivalent ions on Dowex 50, but in this instance approximate methods were used for the computation of the exchange equilibrium constant, and resin activity coefficients were ignored.

The computation of the exchange equilibrium constant requires, in addition to the exchange data themselves, a knowledge of the activity coefficients of the electrolyte solutes in the aqueous phase—or, more precisely, of the appropriate ratio of these coefficients. If the aqueous solutions are sufficiently dilute, this ratio may be taken as unity[6,7]; in somewhat more concentrated solutions, the ratio may be estimated from a modified form of the ionic strength principle.[8] In general, however, it seems preferable to use experimentally determined values of the activity coefficient ratios if such are available. Thus in the case of the silver–hydrogen exchange on Dowex 50, the values of the ratios of activity coefficients of silver nitrate and nitric acid were obtained from independent electromotive force measurements.[12]

The direct determination of the activity coefficients of both electrolyte solutes in a mixed aqueous solution is extremely difficult; it has been ac-

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[1] From part of a thesis submitted by Norman J. Meyer in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Kansas, 1956.

[2] W. J. Argersinger, Jr., A. W. Davidson and O. D. Bonner, *Trans. Kans. Acad. Sci.*, **53**, 404 (1950).

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