CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MICHIGAN STATE UNIVERSITY, EAST LANSING, MICHIGAN 48823

The Kinetics of the Reaction between Perruthenate(VII) and Manganate(VI) in Alkaline Aqueous Media

BY E. V. LUOMA AND C. H. BRUBAKER, JR.

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The rate of the reaction between perruthenate and manganate ions in aqueous alkali has been studied and it is found that the reaction is first order in each reactant and is reversible. The specific reaction rate constant at 20° is 5.7×10^2 M^{-1} sec^{-1} in 0.20 M NaOH. The equilibrium constant for the reaction at 20° is 4.32. The dependence of rate and equilibrium constants on temperature has been measured and the thermodynamic and activation parameters were determined: $\Delta H° = 4.0$ kcal/mole; $\Delta S° = -11$ eu; $E_a = 7.7$ kcal/mole; $\Delta H^* = 7.0$ kcal/mole; $\Delta S^* = -11$ eu; $\Delta G^* = 10$ kcal/mole. The reaction is presumed to proceed by an outer-sphere mechanism and the results are examined with the aid of Marcus' theories.

In the course of a study of the exchange reaction between perruthenate and ruthenate ions,[1] it was noted that the oxidation of manganate by perruthenate was rapid but could probably be studied without resorting to flow or other fast-reaction techniques. Therefore this study was begun with the aim of comparing the results, for what should be an example of a reaction proceeding through an outer-sphere mechanism, with other outer-sphere reactions and with the theories of Marcus.[2]

Experimental Section

Reagents.—Reagent grade chemicals were used throughout this investigation except for LiOH from the Amend Drug and Chemical Co., CsI from the Fairmount Chemical Co., and Rb$_2$-SO$_4$ and ruthenium metal from K & K Laboratories, Inc. Low carbonate (<0.35%) NaOH was used. Water, used for preparation of solutions, had a metal ion content of <1 ppm as NaCl, determined by conductance. Glassware was washed thoroughly with hot commercial bleach, rinsed with distilled water, and air dried.

Perruthenate solutions were prepared by oxidation of Ru^{3+} to RuO$_4$ with NaBiO$_3$ followed by decomposition of RuO$_4$ to RuO$_4^-$ in alkaline solutions of known concentration ($\sim$1 M).[1] A measured volume of each of these solutions was then diluted, after the addition of the measured volume of a sodium salt stock solution, when necessary, to give the desired OH$^-$ and salt concentrations. Manganate solutions were prepared by three methods: (1) fusing MnO$_2$ with NaOH and subsequently diluting to give a manganate stock in 3 M OH$^-$; (2) decomposing KMnO$_4$ in >3 M alkali followed by dilution to the desired OH$^-$ concentration; and (3) dissolving solid K$_2$MnO$_4$ in solutions of the desired OH$^-$ concentration and salt content. Methods 1

and 2 were not suitable for LiOH solutions because Li$^+$ accelerated the decomposition of manganate. Identical kinetic results were obtained from solutions made by all three methods. Perruthenate and manganate solutions were stored in an ice bath.

Analyses.—Spectrophotometry was used to determine the initial concentrations of reactants and to follow the course of the reaction. Molar absorptivities at 20° were determined for perruthenate, ruthenate, permanganate, and manganate solutions at several wavelengths and are listed in Table I and agree with the values of Larsen and Ross and Bennett and Holmes.[3,4] Solutions of each of the anions were found to obey Beer's law up to the highest concentrations studied (5×10^{-4} M).

Procedure.—Samples of each reactant were warmed to 20° and the absorbancies were measured at 385 and 465 mμ for the ruthenium stock and at 507 and 608 mμ for the manganese stock to obtain the concentrations of perruthenate, ruthenate, permanganate, and manganate anions. The absorbancy of the ruthenium stock was also measured at 507 and 608 mμ, depending on which wavelength was to be used for monitoring the reaction. The absorbancies were measured with a Cary Model 14 spectrophotometer which was also used in the rate studies. The Pyrex reaction and spectrophotometer cell was cylindrical, had a capacity of 65 ml and a 10.2-cm light path, and was designed for rapid filling while in position in the thermostated spectrophotometer cell compartment. For each rate determination, a measured volume of each stock solution was pipeted into a separate electrolytic beaker. The beakers were then covered and placed in a constant-temperature bath. When both the reaction cell (in position in the spectrophotometer) and solutions were at the proper temperature, the two reactants were removed from the bath, poured back and forth from one beaker to the other, and then poured quickly into the cell. The spectrophotometer was then started to record the absorbancy vs. time at a fixed wavelength.

The extent of reaction was determined from the net absorbancy change at 608 or 507 mμ. The same kinetic results were

(1) E. V. Luoma and C. H. Brubaker, Jr., Inorg. Chem., **5**, 1618 (1966).
(2) R. A. Marcus, J. Chem. Phys., **24**, 966 (1956); **26**, 867, 872 (1957); **43**, 769 (1965); J. Phys. Chem., **67**, 853 (1963).

(3) R. P. Larsen and L. E. Ross, Anal. Chem., **31**, 176 (1959).
(4) R. M. Bennett and O. B. Holmes, Can. J. Chem., **41**, 108 (1963).

TABLE I

MOLAR ABSORPTIVITIES AT 20°

Wavelength					
Cm^{-1}	mμ	ϵRuO$_4^-$	ϵRuO$_4^{2-}$	ϵMnO$_4^-$	ϵMnO$_4^{2-}$
26,000	385	2150	840	340	1200
24,110	414.7	1075	1075	40	1080
25,500	465	260	1740	395	760
21,150	472.8	250	1720	560	560
19,700	507	170	1120	1805	240
19,000	526	120	610	2395	420
16,500	608	70	30	200	1570

obtained from duplicate samples at each wavelength. Most of the reactions were carried out at 507 mμ because the absorbancy change for a given set of reactants is about 75% greater at 507 than at 608 mμ. Elapsed time was determined from the chart paper and zero time was taken as the time of the first absorbance reading of each experiment.

Competing Reactions.—In addition to the reaction under investigation, there are at least five competing reactions which take place in alkaline solutions of manganate, permanganate, ruthenate, and perruthenate. Perruthenate reacts with OH$^-$ to form RuO$_4^{2-}$;[5] ruthenate disproportionates to form RuO$_2^-$ and RuO$_2 \cdot x$H$_2$O;[6] permanganate reacts with OH$^-$ to form MnO$_4^{2-}$;[7] manganate disproportionates to form MnO$_4^-$ and

the range of 0.2–0.4 M OH$^-$ where the competing reactions were negligible in the times required to reach equilibrium. The equilibrium data at 20° are listed in Table II for

$$K_{eq} = \frac{[RuO_4^{2-}][MnO_4^-]}{[RuO_4^-][MnO_4^{2-}]}$$

It was assumed that the activity coefficients would nearly cancel, and therefore K_{eq} should be thermodynamically valid. The value $E° = 0.037$ v has been calculated from K_{eq}. By use of the value $E° = -0.558$ v[9] for the MnO$_4^{2-}$–MnO$_4^-$ couple, the value $E° = -0.595$ v has been calculated for the RuO$_4^{2-}$–RuO$_4^-$ couple, which is in reasonable agreement with the value of $E° = -0.59$ v determined by Connick and Hurley.[6]

The rate data were found to obey the rate law for second-order, reversible reactions (first order in each reactant). The mathematical form of the rate law is[10]

$$\ln \frac{x + (\beta - q^{1/2})/2\gamma}{x + (\beta + q^{1/2})/2\gamma} = tq^{1/2} + \theta$$

TABLE II

THE EQUILIBRIUM CONSTANT UNDER VARIOUS CONDITIONS

Medium	Initial Concentrations, $M \times 10^5$				Temp, °C	K_{eq}
	[RuO$_4^-$]	[MnO$_4^{2-}$]	[RuO$_4^{2-}$]	[MnO$_4^-$]		
0.405 M NaOH	3.09	4.30	0.12	0.00	20.0	4.37
0.405 M NaOH	4.12	3.23	0.16	0.00	20.0	4.19
0.405 M NaOH	4.12	3.23	0.16	0.00	20.0	4.21
0.405 M NaOH	3.09	4.30	0.12	0.00	20.0	4.03
0.199 M NaOH ⎫ 0.200 M Na$_2$SO$_4$ ⎬	2.52	2.35	0.05	0.02	20.0	4.67
0.199 M NaOH ⎫ 0.200 M Na$_2$SO$_4$ ⎬	2.52	2.35	0.05	0.02	20.0	4.49
0.360 M KOH	4.24	4.73	0.10	0.03	20.0	4.12
0.360 M KOH	4.45	4.41	0.10	0.02	20.0	4.31
0.360 M KOH	4.24	4.73	0.10	0.03	20.0	3.96
0.299 M NaOH	3.15	3.70	0.104	0.00	20.0	4.71
0.299 M NaOH	3.93	2.46	0.13	0.00	20.0	4.16
0.299 M NaOH	3.15	3.70	0.104	0.00	20.0	4.65
0.299 M NaOH	3.13	3.685	0.130	0.018	14.3	Av 4.32 ± 0.25[a]
0.299 M NaOH	3.15	3.70	0.104	0.00	24.7	3.90
0.299 M NaOH	3.93	2.46	0.130	0.00	24.7	4.22
0.299 N NaOH	3.15	3.70	0.104	0.00	24.7	4.11
0.299 N NaOH	3.14	3.67	0.124	0.018	32.0	3.54
0.299 N NaOH	3.92	2.45	0.155	0.012	32.0	3.36
0.299 M NaOH	3.14	3.67	0.124	0.018	32.0	3.57

[a] Standard deviation of the mean.

MnO$_2 \cdot x$H$_2$O;[8] in addition, we have found RuO$_4^{2-}$ begins to oxidize MnO$_4^{2-}$ to MnO$_4^-$ at [OH$^-$] < 0.2 M. At high concentrations of hydroxide (>0.6 M) decomposition of MnO$_4^-$ to MnO$_4^{2-}$ caused errors estimated at 10% in the kinetic results of this investigation.

Results

The reaction under investigation was found to be reversible. Because of the competing reactions, the equilibrium constant could be determined only over

where β, q, γ, and θ are functions of the initial concentrations of reactants and products and of the rate constants for the forward and reverse reactions.

$$q = \beta^2 - 4\alpha\gamma = k_1^2(A_0 - B_0)^2 + k_2^2(C_0 - D_0) + 2k_1k_2[(A_0 + B_0)(C_0 + D_0) + 2A_0B_0 + 2C_0D_0]$$

$$\theta = \ln \frac{\beta - q^{1/2}}{\beta + q^{1/2}}$$

$$\alpha = k_1(A_0B_0) - k_2(C_0D_0)$$

(5) A. Carrington and M. C. R. Symons, *J. Chem. Soc.*, 284 (1960).
(6) R. E. Connick and C. R. Hurley, *J. Am. Chem. Soc.*, **74**, 5012 (1952).
(7) B. Jezowska-Trzebiatowska and J. Kalecinski, *Bull Acad. Polon. Sci.,* Ser. Sci. Chim., Geol., Geograph., **7**, 405 (1959).
(8) B. Jezowska-Trzebiatowska and J. Kalecinski, *ibid.,* **7**, 411 (1959).

(9) A. Carrington and M. C. R. Symons, *J. Chem. Soc.*, 3373 (1956).
(10) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 29.

$$\beta = -(k_1 A_0 + k_1 B_0 + k_2 C_0 + k_2 D_0)$$

$$\gamma = k_1 - k_2$$

A_0, B_0, C_0, and D_0 are the initial concentrations of the MnO_4^{2-}, RuO_4^-, MnO_4^-, and RuO_4^{2-}, respectively. The rate constant for the forward reaction was determined by a least-squares fitting of the data to the above equation with the Michigan State University Control Data 3600 computer. The standard deviation of the individual data points from the calculated curve was within the limit of spectrophotometric accuracy. In the various experiments, the initial concentrations of RuO_4^- ranged from 1.24 to 8.93 $\times$ 10^{-5} M, MnO_4^- from 0.90 to 7.82 $\times$ 10^{-5} M, RuO_4^{2-} from 0.00 to 1.92 $\times$ 10^{-5} M, and MnO_4^- from 0.00 to 0.56 $\times$ 10^{-5} M. The rate was found to be dependent on both the concentration and the size of the cation. Table III is a summary of the rate determinations at 20.0° in various alkaline aqueous media.

TABLE III

THE RATE IN VARIOUS AQUEOUS ALKALINE MEDIA AT 20°

Cation	Hydroxide	Other anion	$10^{-2}k_r$, M^{-1} sec^{-1}
0.189 Li$^+$	0.189		5.48 $\pm$ 0.14^a
0.379 Li$^+$	0.379		6.70 $\pm$ 0.29
0.946 Li$^+$	0.946		9.53 $\pm$ 0.86
0.101 Na$^+$	0.101		4.77 $\pm$ 0.33
0.202 Na$^+$	0.202		5.73 $\pm$ 0.33
0.299 Na$^+$	0.299		7.22 $\pm$ 0.26
0.405 Na$^+$	0.405		7.66 $\pm$ 0.09
0.608 Na$^+$	0.608		9.32 $\pm$ 0.34
0.697 Na$^+$	0.697		10.6 $\pm$ 1.1
1.01 Na$^+$	1.01		10.9 $\pm$ 0.4
0.399 Na$^+$	0.199	0.100 SO$_4^{2-}$	6.82 $\pm$ 0.10
0.599 Na$^+$	0.199	0.200 SO$_4^{2-}$	9.17 $\pm$ 0.30
0.799 Na$^+$	0.199	0.300 SO$_4^{2-}$	10.3 $\pm$ 0.4
0.799 Na$^+$	0.199	0.200 PO$_4^{3-}$	9.04 $\pm$ 0.30
0.799 Na$^+$	0.199	0.600 NO$_3^-$	9.98 $\pm$ 0.20
0.799 Na$^+$	0.199	0.600 ClO$_4^-$	10.3 $\pm$ 0.4
0.090 K$^+$	0.090		6.15 $\pm$ 0.04
0.180 K$^+$	0.180		7.93 $\pm$ 0.14
0.360 K$^+$	0.360		10.4 $\pm$ 0.2
0.720 K$^+$	0.720		15.2 $\pm$ 0.8
0.199 Na$^+$ 0.100 Rb$^+$	0.199	0.050 SO$_4^{2-}$	8.34 $\pm$ 0.03
0.199 Na$^+$ 0.200 Rb$^+$	0.199	0.100 SO$_4^{2-}$	10.2 $\pm$ 0.5
0.199 Na$^+$ 0.100 Cs$^+$	0.199	0.050 SO$_4^{2-}$	11.0 $\pm$ 0.2
0.199 Na$^+$ 0.200 Cs$^+$	0.199	0.100 SO$_4^{2-}$	14.6 $\pm$ 0.8

^{a} Standard deviation of the mean.

The rate of reaction was found to be relatively insensitive to ionic strength. Examination of the data in Table IV shows that there is, if anything, a slight decrease in rate with an increase in ionic strength, when the concentration of cation is held constant. The accuracy of the rate data does not permit determining whether the decrease is significant.

The equilibrium constant is markedly temperature

TABLE IV

DEPENDENCE OF THE RATE ON IONIC STRENGTH
IN SODIUM HYDROXIDE SOLUTIONS AT 20.0°

Hydroxide	Anion	Na$^+$	μ	k, M^{-1} sec^{-1}
0.405		0.405	0.405	766 $\pm$ 9^a
0.199	0.100 SO$_4^{2-}$	0.399	0.499	682 $\pm$ 10
0.608		0.608	0.608	932 $\pm$ 34
0.199	0.200 SO$_4^{2-}$	0.599	0.799	917 $\pm$ 30
0.199	0.600 NO$_3^-$	0.799	0.799	998 $\pm$ 30
0.199	0.600 ClO$_4^-$	0.799	0.799	1029 $\pm$ 30
0.199	0.300 SO$_4^{2-}$	0.799	1.099	1029 $\pm$ 37
0.199	0.200 PO$_4^{3-}$	0.799	1.399	903 $\pm$ 30

Concentrations, M

^{a} Standard deviation of the mean.

TABLE V

DEPENDENCE OF THE RATE ON TEMPERATURE IN
0.299 M NaOH

[RuO$_4^-$]	[MnO$_4^{2-}$]	[RuO$_4^{2-}$]	[MnO$_4^-$]	Temp, °C	k_r, M^{-1} sec^{-1}
3.13	3.685	0.130	0.018	14.3	572
3.92	2.455	0.163	0.012	14.3	587
3.13	3.685	0.130	0.018	14.3	573
3.92	2.455	0.163	0.012	14.3	576
4.23	2.71	0.00	0.01	20.0	714
5.64	2.03	0.00	0.01	20.0	735
2.82	3.39	0.00	0.01	20.0	683
3.15	3.70	0.10	0.00	20.0	737
3.15	3.70	0.10	0.00	20.0	742
3.15	3.70	0.104	0.00	24.7	902
3.93	2.46	0.130	0.00	24.7	905
3.15	3.70	0.104	0.00	24.7	904
3.92	2.45	0.155	0.12	32.0	1227
3.14	3.67	0.124	0.018	32.0	1301

Initial concentrations, $M \times 10^5$

dependent. From the data in Table II, the enthalpy of reaction is -4.0 kcal/mole, and the entropy, -11 eu.

The temperature dependence of the rate was studied in 0.30 M NaOH. The activation energy, E_a, is 7.7 kcal/mole, and $\Delta H^* = 7.0$ kcal/mole, $\Delta S^* = -11$ eu, and $\Delta G^* = 10$ kcal/mole.

Discussion

The value obtained for $\Delta S°$ was not anticipated. The entropy change for the reaction

$$RuO_4^- + MnO_4^{2-} \rightleftharpoons RuO_4^{2-} + MnO_4^- \qquad (1)$$
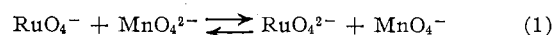
was expected to be near zero. A value $S° = 1.7$ eu for the above reaction is calculated from the empirical formula[11]

$$S°(MO_n^-) = 40.2 + \frac{3}{2}R \ln A - \frac{27.2Z}{0.25nr_0} \qquad (2)$$

where n = number of "bare" oxygen atoms, Z = charge on the anion, A = molecular weight of the anion, and r_0 = M–O distance[12] $+ 1.40$ A. The experimental result of $\Delta S° = -11$ eu is probably much too different from the calculated value of $\Delta S° = 1.7$ eu to attribute to experimental error (even considering an

(11) A. M. Couture and K. J. Laidler, *Can. J. Chem.*, **35**, 202 (1957).
(12) Mn–O and Ru–O distances were taken from (a) J. C. Sheppard and A. C. Wahl, *J. Am. Chem. Soc.*, **79**, 1920 (1957); (b) R. C. L. Mooney, *Phys. Rev.*, **37**, 1306 (1931); (c) M. D. Silverman and H. A. Levy, *J. Am. Chem. Soc.*, **76**, 3317 (1954).

average deviation of 3.6 eu[11]). It was suggested that one or more of the anions could possibly have hydroxide ion associated with them.[13] Hydroxide ion association can be represented by the equilibrium

$$MO_4{}^{x-} + OH^- \rightleftharpoons MO_4OH^{(x+1)-} \qquad (3)$$
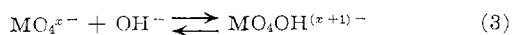
where M is Ru or Mn and x is 1 or 2, depending on the oxidation state. The negative value of $\Delta S°$ suggests that the equilibrium constants for reaction 3 are larger for ruthenate and permanganate than for perruthenate and manganate. The equilibrium constant for reaction 3 should also be larger for permanganate than ruthenate because of size and charge contributions to electrostatic repulsion. If the formation constant for $MO_4OH^{(x+1)-}$ is large, no effect of varying $[OH]^-$ would be noted in the range of base concentrations which could be studied.

Comparison of the experimental rate constant with the rate constants calculated from Marcus' equations is of interest.[2] From Marcus' equations and a solution of 0.20 ionic strength: $k_r = 7.8 \times 10^4\ M^{-1}\ sec^{-1}$ ($r = 5.76$ A, the sum of the crystal radii[12]); $k_r = 6.2 \times 10^7\ M^{-1}\ sec^{-1}$ ($r = 10.14$ A, water molecule interposed). The experimentally determined rate constant for reaction in 0.20 M sodium hydroxide solution was (Table III): $k_r = 5.7 \times 10^2\ M^{-1}\ sec^{-1}$. The agreement between the experimental value and the calculated value for $r = 5.76$ A is probably as good as can be expected. The estimate of the rearrangement energy is undoubtedly low, especially in view of the possible hydroxide ion association with one or more of the anions. An increase in rate by a factor of 1.10 is predicted from Marcus' equations for a change in ionic strength from 0.405 to 0.499 but was not observed (Table IV). There may actually be a slight decrease in rate with increasing ionic strength (by changing the nature of the anion) at constant sodium and hydroxide concentrations, but the decrease is small and may be due to experimental error. The observed rate of reaction is probably affected by both ion pairing between alkali metal ions and the reactants and association of those anions with hydroxide. At present, one cannot assess the above contributions to the rate.

A comparison of the results from this investigation with those obtained from the manganate–permanganate[12a] and ruthenate–perruthenate systems is worthwhile. In the manganate–permanganate exchange reaction Sheppard and Wahl found for 0° and 0.16 M sodium hydroxide $k_r = 710\ M^{-1}\ sec^{-1}$; in the ruthenate–perruthenate exchange reaction, a value of $k_r > 10\ M^{-1}\ sec^{-1}$ for 0° and 0.10 M sodium hydroxide was estimated. For the "mixed" system of manganate–perruthenate a value of $k_r = 220\ M^{-1}\ sec^{-1}$ is calculated for 0° and 0.20 M sodium hydroxide from the rate obtained at 20° and $E_a = 7.65$ kcal/mole. We note that the manganate–perruthenate reaction is slower than either of the two exchange reactions.

The m factor in the Marcus theory suggests a higher rate for the manganate–perruthenate reaction since $\Delta G°$ is negative, whereas the value of $\Delta G°$ for exchange is about zero. On the other hand, the manganate–perruthenate reaction may have a higher energy of rearrangement which would cause a lower rate of reaction. In addition, the electronic vibrational levels of the ruthenium and manganese species do not coincide so that the transmission probability for the electron within the activated complex for manganate–perruthenate is probably lower than the transmission probability in either ruthenate–perruthenate or manganate–permanganate. The lower rate in the manganate–permanganate system in comparison to ruthenate–perruthenate might be attributed to the association of permanganate with hydroxide. Hydroxide association is consistent with the negative value found for $\Delta S°$ in the manganate–perruthenate equilibrium.

From the theory we calculate $m^2\mu = 7.6$ and from the experimental $\Delta G^*\ m^2\mu = 9.6$ kcal/mole. The larger "observed" value suggests a fairly large reorganization energy and agrees with either OH^- association or coordination sphere expansion.

The values of the activation energy, the entropy, and the free energy of activation for the manganate–permanganate[12a] reaction are $E_a = 10.5$ kcal, $\Delta S^* = -9$ eu, and $\Delta G^* = 12.4$ kcal/mole for 0° and 0.16 M sodium hydroxide solution. For manganate–perruthenate, $\Delta E_a = 7.6$ kcal, $\Delta S^* = -11$ eu, and $\Delta G^* = 10$ kcal/mole at 20.0° in 0.30 M sodium hydroxide solution. The differences might be attributed, in part, to experimental error and to the different OH^- concentrations. One would expect, as is found, that the entropy of activation is more negative for the manganate–perruthenate system.

A comparison of the cation effect in the manganate–permanganate and manganate–perruthenate reactions shows that the former is more sensitive to the size and concentration of the cation. For example, increasing the sodium ion concentration from 0.16 to 0.99 M increases the rate of the manganate–permanganate reaction by a factor of 2.4. In the manganate–perruthenate reaction, a similar increase in sodium ion concentration (0.20 to 1.0 M) increases the rate of reaction by a factor of 2.1. Similarly, the reaction rate in manganate–permanganate is nearly doubled by changing from 0.57 M sodium to 0.57 M potassium ion. The rates of reaction for similar concentrations, interpolated from the rate data (Table III), indicate that potassium ion is only 40% more effective than sodium ion in the manganate–perruthenate reaction. The entropy of reaction of the manganate–perruthenate reaction, -11 eu, is essentially the same as the entropy of activation. Considering experimental error, it is possible to estimate that the difference between the two entropies is at most 2 eu. Thus, the major part of the entropy of activation is the entropy of reaction, which is probably not unreasonable when one considers that the reaction is slower than predicted by Marcus' equations.

(13) A referee has suggested that a change in coordination number on oxidation of RuO₄⁻ to something like Ru(H₂O)₂O₄²⁻ could also account for the observed entropy change, but we would not expect RuO₄⁻–Ru(H₂O)₂O₄²⁻ exchange to be rapid in that case.

The Topology of Phase Diagrams of Reciprocal Molten Salt Systems

BY MILTON BLANDER AND L. E. TOPOL

Liquidus temperatures in the reciprocal molten salt system Li,K‖F,Cl are calculated from the conformal ionic solution theory, and the calculated topology of the solid–liquid equilibria is in excellent correspondence with the measurements of Berezina, Bergman, and Bakumskaya. The influence of parameters in the theory on the topology of the solid–liquid phase diagram is discussed. An approximate relation which may be used to predict immiscibility gaps in reciprocal systems is given (eq 16) and is shown to provide a simple and fundamental basis for many of the empirical rules stated by previous workers.

The phase diagrams of a large number of simple molten reciprocal salt systems[1] have been investigated. The topology and characteristics of the solid–liquid equilibria in these systems have been empirically characterized and classified by Russian workers[2] in terms of factors such as the difference in free energies between the stable and unstable solid salt pairs, the polarizabilities of the ions, and electronic structure. In this paper we will apply a recent statistical mechanical theory,[3] the conformal ionic solution theory, to reciprocal salt systems and show that there is a fundamental justification for some of the empirical and less general correlations of the Russian school. Our discussion will be illustrated by calculations of liquidus temperatures in the system Li,K‖F,Cl and it will be demonstrated that the calculations from the theory with the aid of only one unknown parameter, which is adjustable within narrow limits, can reproduce all of the measured topological features of the phase diagram quite accurately. It is believed that this is an extreme test of the theory because the liquidus temperatures and topology of phase diagrams are extremely sensitive, both to small changes in the magnitude of the parameters in the theory and to the form of the equations used. We will discuss how variations in the thermodynamic quantities which enter into the theory influence the calculated phase diagram and show the relationship of these quantities to the features discussed by the Russian workers. The theory cannot be utilized to give detailed predictions of liquidus temperatures *a priori*. We hope to show, however, that topological features of phase diagrams are related to macroscopic thermodynamic quantities in the theory. These quantities, in turn, can be related to microscopic ionic interactions. Thus, it is hoped that this discussion will be a useful guide in predicting topological features and in extracting information from the large number of phase diagrams which have been published. In conclusion, we will apply the theory to the occurrence of miscibility gaps which have been extensively studied and discussed in the Russian literature.[4]

The Theory of Conformal Ionic Solutions.—The theory of conformal ionic solutions has been extended to reciprocal salt systems.[3] The expression derived for the total excess free energy of mixing (ΔG^E_m) of the three salts AC, BC, and BD is[5]

$$\Delta G^E_m = X_A X_D \Delta G^\circ + X_D \Delta G^E_{12} + X_C \Delta G^E_{34} + X_A \Delta G^E_{13} + X_B \Delta G^E_{24} + X_A X_B X_C X_D \Lambda \quad (1)$$

where the X's are ion fractions. For example, the cation fraction of A is $X_A = n_A/(n_A + n_B)$ and the anion fraction of C is $X_C = n_C/(n_C + n_D)$, where the n's are the number of moles of the ions indicated. ΔG° is the standard molar Gibbs free energy change for the metathetical reaction

$$AC(l) + BD(l) \rightleftharpoons AD(l) + BC(l) \quad (2)$$

ΔG^E_{ij} is the excess free energy of mixing of the binary mixture of the salts i and j where AD is salt 1, BD is 2, AC is 3, and BC is 4. Although it has been shown that the terms in ΔG^E_{ij} are general,[3] in this paper we will include only second-order terms so that

$$\Delta G^E_{12} = X_A X_B \lambda_{12} \quad (3a)$$

$$\Delta G^E_{13} = X_C X_D \lambda_{13}, \text{ etc.} \quad (3b)$$

where λ_{ij} is an energy parameter depending solely on

(1) A simple reciprocal salt system is one containing two cations and two anions.

(2) (a) A. G. Bergman, K. A. Evdokimova, and O. F. Bogush, *Izv. Sektora Fiz.-Khim. Analiza, Inst. Obshch. Neorgan. Khim., Akad. Nauk SSSR*, **27**, 419 (1956); (b) J. E. Ricci, "Phase Diagrams of Fused Salts," in "Molten Salt Chemistry," M. Blander, Ed., Interscience Publishers, New York, N. Y., 1964, p 239.

(3) M. Blander and S. J. Yosim, *J. Chem. Phys.*, **39**, 2610 (1963).

(4) (a) I. N. Belyaev, *Usp. Khim.*, **29**, 899 (1960); *Russ. Chem. Rev.*, **29**, 428 (1960); (b) M. L. Sholokhovich, D. S. Lesnykh, G. A. Bukhalova, and A. G. Bergman, *Dokl. Akad. Nauk SSSR*, **103**, 261 (1955).

(5) M. Blander and L. E. Topol, *Electrochim. Acta*, **10**, 1161 (1965). (It should be noted that we have replaced the Helmholtz free energy in this reference by the Gibbs free energy. The difference is not significant in this second-order equation.)