the addition of an aqueous $[(n\text{-}C_4H_9)_4N]Cl$ solution to an aqueous solution of K_2ReCl_6 at room temperature. The resulting pale green precipitate was washed with water and dried in vacuo. $ReOCl_3(PPh_3)_2$ was prepared by the method of Chatt and Rowe.[11] All reactions were carried out under a positive pressure of nitrogen with a mercury bubbler system so as to increase the boiling point of PhCOCl to 209 °C. The bubbler consisted of a cylindrical glass reservoir (22-mm internal diameter) containing 40 mL of mercury and fitted with a 4-mm diameter gas inlet tube extending 95 mm into the mercury pool.

A. Reactions of $KReO_4$ with PhCOCl. (i) $Re_2(O_2CPh)_2Cl_4$. $KReO_4$ (1.0 g, 3.5mmol) was refluxed in PhCOCl (15 mL, 13 mmol) for 5 h. The resulting solid was filtered off and washed with PhCOCl and petroleum ether and dried. It was then washed several times with water to dissolve the yellow-green component K_2ReCl_6 (vide infra). The resulting emerald green solid was finally washed with propanol and petroleum ether and dried in vacuo; yield 50% (0.65 g). Anal. Calcd for $C_{14}H_{10}Cl_4O_4Re_2$: C, 22.23; H, 1.33. Found: C, 21.86; H, 1.48. IR data (cm^{-1}): ν(Re–Cl) = 327 (s), ν(COO) = 1416 (vs, br). Electronic absorption spectral data in methanol (nm): 815 (w), 630 (w), 355 (m), 314 (s, sh), 287 (vs).

(ii) K_2ReCl_6. The water washings from preparation i were collected and evaporated to dryness. The resulting yellow-green crystals were then washed with EtOH and diethyl ether and finally dried in vacuo; yield 43% (0.71 g). The spectral properties of this compound were identical with those of an authentic sample of K_2ReCl_6.

(iii) $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$. $KReO_4$ (1.0 g, 3.5 mmol) was refluxed in PhCOCl (15 mL, 13 mmol) for 5 h, the reaction mixture was cooled, and a HCl(g) saturated solution of $[(n\text{-}C_4H_9)_4N]Br$ (3.0 g, 9.6 mmol) dissolved in ethanol (50 mL) was added. This mixture was refluxed for an additional 1 h, the solution evaporated to low volume and diethyl ether (100 mL) added. The resulting solid was filtered off and washed with ethanol and diethyl ether. So that the K_2ReCl_6 which is present could be removed, the product was added to hot methanol and the mixture filtered into concentrated hydrochloric acid. The blue solution was then evaporated by boiling until blue crystals of $[n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ formed. These were filtered off, washed with ethanol (10 mL) and diethyl ether, and dried in vacuo; yield 56% (1.1 g). Anal. Calcd for $C_{32}H_{72}Cl_8N_2Re_2$: C, 33.69; H, 6.36. Found: C, 33.86; H, 6.12. [IR data: ν(Re–Cl) = 335 cm^{-1} (s).] The electronic absorption spectrum of a methanol solution of this complex was identical with that reported in the literature.[1]

B. Reaction of $[(n\text{-}C_4H_9)_4N]ReO_4$ with PhCOCl. $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$. In a typical reaction, $[(n\text{-}C_4H_9)_4N]ReO_4$ (3.0 g, 6.1 mmol) was refluxed with PhCOCl (30 mL, 26 mmol) for 1.5 h and cooled, and an HCl(g) saturated solution of $[(n\text{-}C_4H_9)_4N]Br$ (5.0 g, 16 mmol) dissolved in ethanol (75 mL) was added. After a reflux period of 1 h, the solution was evaporated to approximately half-volume under a stream of nitrogen. The resulting blue crystals were filtered off, washed with 10 mL portions of ethanol and then with diethyl ether, and dried in vacuo; yield 92% (3.19 g). The product so obtained is of sufficient purity that it can be used without further recrystallization. The spectral properties of this complex were identical with those described in the literature.[1] Anal. Calcd for $C_{32}H_{72}Cl_8N_2Re_2$: C, 33.69; H, 6.36. Found: C, 33.97; H, 6.12.

C. Reactions of $ReOCl_3(PPh_3)_2$ with PhCOCl. (i) *trans*-$ReCl_4(PPh_3)_2$. $ReOCl_3(PPh_3)_2$ (1.0 g, 1.2 mmol) was refluxed in PhCOCl (15 mL, 13 mmol) for 5 min. The deep red solution was filtered, and the resulting insoluble red solid was washed with diethyl ether and dried in vacuo; yield 43%. The spectral properties of this compound were identical with those reported previously.[12]

(ii) $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$. $ReOCl_3(PPh_3)_2$ (1.0 g, 1.2 mmol) was reacted with PhCOCl as described in preparation iii of section A; yield 70% (0.48 g).

D. Reaction of $[(n\text{-}C_4H_9)_4N]_2ReCl_6$ with PhCOCl. $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$. $[(n\text{-}C_4H_9)_4N]_2ReCl_6$ (1.5 g, 1.7 mmol) was reacted as described in B; yield 95% (0.92 g).

E. Reaction of $ReCl_4(PPh_3)_2$ with PhCOCl. $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$. Following the procedure given in preparation iii of section A, *trans*-$ReCl_4(PPh_3)_2$ (0.50 g, 0.6 mmol) was converted to $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ in 80% yield (0.26 g).

F. Reactions of Molybdenum Oxo Species with PhCOCl. (i) A mixture of $MoO_2(acac)_2$ (0.33 g, 1.0 mmol) and PhCOCl (15 mL, 13 mmol) was refluxed for 2 h. The solution was cooled, and an HCl(g)-saturated solution of $[(n\text{-}C_4H_9)_4N]Br$ (1.5 g, 4.7 mmol) dissolved in ethanol (35 mL) was added. An additional reflux period of 2 h produced a dark red solution which was evaporated to half-volume under a stream of nitrogen. An excess of diethyl ether (50 mL) was then added, and the green crystals of $[(n\text{-}C_4H_9)_4N]MoOCl_4$ were filtered off, washed with diethyl ether, and dried in vacuo; yield 76% (0.38 g). The spectroscopic properties of this product were identical with those reported in the literature.[13]

(ii) K_2MoO_4 (0.24 g, 1.0 mmol) when reacted as in preparation i above afforded $[(n\text{-}C_4H_9)_4N]MoOCl_4$ in 84% yield (0.42 g).

Physical Measurements. Infrared spectra were recorded from 4000 to 400 cm^{-1} with KBr plates and from 400 to 200 cm^{-1} with polyethylene on a Beckman IR 12 spectrophotometer. Electronic absorption spectra were obtained in the region from 900 to 300 nm with a Varian 634 spectrophotometer. Elemental microanalytical data were obtained by Dr. C. S. Yeh of this department.

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Registry No. $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$, 14023-10-0; $KReO_4$, 10466-65-6; PhCOCl, 98-88-4; $Re_2(O_2CPh)_2Cl_4$, 81011-79-2; $[(n\text{-}C_4H_9)_4N]ReO_4$, 16385-59-4; $ReOCl_3(PPh_3)_2$, 17442-18-1; *trans*-$ReCl_4(PPh_3)_2$, 34248-10-7; $[(n\text{-}C_4H_9)_4N]_2ReCl_6$, 71128-58-0; $MoO_2(acac)_2$, 17524-05-9; $[(n\text{-}C_4H_9)_4N]MoOCl_4$, 19341-30-1; K_2MoO_4, 13446-49-6.

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Contribution from the Chemistry Division, Naval Research Laboratory, Washington, D.C. 20375

Solubility of Manganese Oxide in Molten Sodium Chloride and Sodium Sulfate

L. M. Deanhardt, Kurt H. Stern,*[1] and Scott R. Wolff[2]

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Manganese is a reactive element that has potential for increasing the oxidation resistance of superalloys. Specifically, Mn is thought to reduce CrO_3 volatilization by formation of $MnCr_2O_4$ spinel.[3] The question of whether manganese might improve hot corrosion resistance was approached in the present work by measuring the solubility of manganese oxide in molten Na_2SO_4 and NaCl. Valuable insight concerning the hot corrosion resistance conferred by several metal constituents of superalloys was reported recently by measurement of the solubility of the oxides of these metals in molten Na_2SO_4 and NaCl.[4,5,8,9]

In previous solubility studies[4,5] of the oxides of nickel, cobalt, and yttrium we have used a coulometric titration technique[6,7] developed in our laboratory, in which a solution of the respective salt, e.g., $NiSO_4$ in Na_2SO_4, is titrated with oxide ion (O^{2-}) generated coulometrically at a stabilized zirconia electrode. However, this method proved to be unsuitable for

(1) To whom correspondence should be addressed.
(2) Undergraduate student, James Madison University; summer research participant at the Naval Research Laboratory.
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studying manganese oxide solubility because $MnCl_2$–NaCl (830 °C) and $MnSO_4$–Na_2SO_4 (930 °C) solutions were found to be unstable. We have therefore used a potentiometric technique in which the appropriate oxide and molten salt are equilibrated, the oxide activity is measured potentiometrically, and the metal is determined from quenched melt samples by standard analytical techniques. A similar technique was used by Rapp and co-workers[8,9] to measure the solubility of Al_2O_3, Cr_2O_3, NiO, and CoO in molten Na_2SO_4.

Experimental Section

Stability Range of Manganese Oxides. An important question to be addressed is the stoichiometry of the oxide whose solubility is to be measured. According to the most recent critical review[10] of thermodynamic data for manganese compounds, Mn_2O_3 is the stable oxide at 0.2 atm of O_2 from 477 to 1027 °C. However, a more recent experimental study of manganese oxide equilibria[11] shows that Mn_2O_3 transforms to Mn_3O_4 at 879 °C in air. We have confirmed this latter result by heating Mn_2O_3 thermogravimetrically (Mettler thermogravimetry apparatus), observing the expected weight loss, cooling the oxide under vacuum, and identifying the resulting Mn_3O_4 by its X-ray powder pattern. Therefore, the oxide whose solubility is measured in NaCl at 830 °C is Mn_2O_3 and in Na_2SO_4 at 930 °C is Mn_3O_4.

Stability of Manganese Melts. The 20 wt % melts of $MnCl_2$ in NaCl and $MnSO_4$ in Na_2SO_4 were prepared from high-purity anhydrous manganese salts (Alfa Inorganics) and vacuum-dried (450 °C) alkali-metal salts in a glovebox (Vacuum Atmospheres Corp.) filled with a dry and CO_2-free 20% O_2-in-helium mixture. The respective mixtures were heated in porcelain crucibles for 30 h, and the remaining material was then analyzed by X-ray diffraction. In the chloride system only Mn_2O_3 was observed; in the sulfate system, although some Mn_2SO_4–Na_2SO_4 melt remained, oxide was found at the upper edge of the crucible. Since the melts were unstable, coulometric titrations, as previously carried out for the nickel, cobalt, and yttrium systems, could not be performed.

Solubility of Manganese Oxides. In a glovebox containing 20% O_2, samples of Mn_2O_3 in NaCl and Mn_3O_4 in Na_2SO_4 were equilibrated in high-purity (99.8%) alumina crucibles. The oxide activity was monitored by using the cell

$$\text{Ag}|\text{melt} + \text{AgCl or } Ag_2SO_4\ (10\text{m/o})|Na^+ \text{ mullite}|\text{NaCl or } Na_2SO_4 + Na_2O|\text{stab. } ZrO_2|O_2|\text{Pt} \quad (1)$$

The details and interpretation of this measurement were fully discussed elsewhere.[7] After 20 h the EMF became constant, indicating that equilibrium had been achieved. The melt was then sampled at intervals of ~3 h by dipping a cold, high-purity alumina rod into the melt and quickly withdrawing it. The adhering frozen melt was analyzed by atomic absorption (Perkin-Elmer Model 360) and atomic emission (Spectrospan III D.C. argon plasma spectrometer). Results of the two methods were in good agreement.

Results and Discussion

Based on the known chemistry of manganese compounds,[12] the solution reactions are

$$Mn_2O_3(s) + 4NaCl(l) = 2MnCl_2(sol) + 2Na_2O(sol) + {}^1/_2O_2(g) \quad (2)$$

$$Mn_3O_4(s) + 3Na_2SO_4(l) = 3MnSO_4(sol) + 3Na_2O(sol) + {}^1/_2O_2(g) \quad (3)$$

Note that in both reactions the solution reaction involves a valence change for manganese and that the solubility depends on the O_2 pressure.

Since the EMF of cell is directly related to the activity of Na_2O, and manganese is expressed as a concentration, it was necessary to convert the oxide activity to concentration (mole fraction scale). The required activity coefficients, 1.7×10^{-4} in NaCl and 4.5×10^{-4} in Na_2SO_4 (on a mole fraction scale) were measured previously.[4] For reaction 2 the experimentally determined equilibrium constant is

$$K_x = X_{MnCl_2}{}^2X_{Na_2O}{}^2P_{O_2}{}^{1/2} = (6.6 \pm 2.2) \times 10^{-23}$$

and for reaction 3

$$K_x = X_{MnSO_4}{}^3X_{Na_2O}{}^3P_{O_2}{}^{1/2} = (9.5 \pm 2.5) \times 10^{-30}$$

assuming $X_{NaCl} = X_{Na_2SO_4} = 1$ in these dilute melts. The values of K_x above are average values with the uncertainty given as a standard deviation. The thermodynamic equilibrium constants of reactions 2 and 3 can be calculated from the Gibbs energies of formation given in Table I. From these data, $K_2 = 1.56 \times 10^{-34}$, and $K_3 = 2.86 \times 10^{-48}$. A comparison of the thermodynamic constants with the respective K_x's gives the activity coefficient of the manganese salts: $K_2/K_{x_2} = (\delta_{MnCl_2}\delta_{Na_2O})^2$, $K_3/K_{x_3} = (\delta_{MnSO_4}\delta_{Na_2O})^3$. Since δ_{Na_2O} is known, this relationship gives $\delta_{MnCl_2} = 9.0 \times 10^{-3}$ in NaCl and $\delta_{MnSO_4} = 1.5 \times 10^{-3}$ in Na_2SO_4. These values are similar to previously reported activity coefficients of $NiCl_2$ and $CoCl_2$ in NaCl and $NiSO_4$ and $CoSO_4$ in Na_2SO_4.[3] A comparison of the solubilities of the manganese oxides with those of the oxides of nickel,[4] cobalt,[4] and yttrium[5] shows that under an ambient oxygen pressure they are all equal to within 1 order of magnitude. Any marked differences exhibited by the oxides in conferring corrosion resistance is therefore likely to involve factors other than solubility.

Table I

	$G°_f$, kcal mol^{-1}		
	1100 K	1200 K	ref
NaCl(l)	−74.268		13
Na_2SO_4(l)		−212.612	13
Na_2O(l)	−61.126	−58.089	13
Mn_2O_3(s)	−160.75		10
Mn_3O_4(s)		−230.4	10
$MnCl_2$(l)	−82.7		10
$MnSO_4$(l)		−145.3	10

Registry No. Mn_2O_3, 1317-34-6; Mn_3O_4, 1317-35-7; NaCl, 7647-14-5; Na_2SO_4, 7757-82-6.

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Contribution from the Departments of Chemistry, University of Northern Iowa, Cedar Falls, Iowa 50614, and Northern Illinois University, DeKalb, Illinois 60115

Tetraamine Complexes of Chromium(III). 4. Kinetics of the Aquation of the *cis*-Aquabis(ethylenediamine)iodochromium(III) Cation

James C. Chang*[1a] and Joe W. Vaughn*[1b]

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Although the kinetics of the aquation of the *cis*-dichloro-, *cis*-dibromo-, *cis*-aquachloro-, and *cis*-aquabromobis(ethylenediamine)chromium(III) cations have been extensively studied,[2-7] there is no indication of similar studies of the

(1) (a) University of Northern Iowa. (b) Northern Illinois University.
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