adsorbed more strongly by manganese and iron than by nickel according to Trapnell.[8]

Discussion

Catalysis at the interface between solids and fluids is a complex phenomenon, dependent on a number of parameters. For instance, it can be expected that the adsorption of N_3^- and K^+ alters the work function of the metal catalyst. Nevertheless, considerations based on the work functions of the metals do not seem to lead to an understanding of the catalytic activities observed in this work.

The data contained in this paper seem to indicate that holes in the d-band of the catalyst (free electron theory) or singly occupied atomic d-orbitals (valence bond theory) are important for catalytic action. Reactions affected by the rate of formation of a chemisorbed positive ion (electron transfer to the catalyst) or a covalent substrate–catalyst bond are favored by the presence of holes in the d-band. The formation of N_3^+ ions is energetically impossible under the conditions of KN_3 decomposition. However, it seems a likely possibility that N_3^- ions which have sufficient excitation energy form a partly covalent bond with the catalyst. This bond will be relatively strong with manganese, iron, cobalt, and nickel since singly occupied atomic d-orbitals are available. With copper this is not the case and the bond can be formed only with the unused fraction of surface bonding orbitals. This seems to explain the higher catalytic activity of manganese, iron, cobalt, and nickel as compared with copper. Two N_3 groups, chemisorbed on adjacent sites of the catalyst surface, may react to yield three molecules of nitrogen while two potassium ions may become reduced to potassium metal.

Acknowledgment.—The author wishes to thank Dr. B. deB. Darwent for his comments on this paper and Mr. M. D. Kemp for supplying the KN_3 used in the experiments.

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[8] B. M. W. Trapnell, *Proc. Roy. Soc.* (London), **A218**, 566 (1953).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Precipitation of Silver(I) Halides in Molten Lithium Nitrate–Potassium Nitrate Eutectic[1]

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Using a glass reference electrode, the precipitation of AgCl, AgBr, and AgI in $LiNO_3$–KNO_3 eutectic was studied by a potentiometric titration technique. Titrations were performed at a series of temperatures and solubility products and other thermodynamic properties were calculated for the reaction: $Ag^+ + X^- \rightleftharpoons AgX(s)$. Employing a method suggested by Gurney, the entropy associated with the co-sphere of each anion was calculated for aqueous solution and for the molten solution. By comparing these unitary entropy terms, it can be shown that the interaction between molten solvent and halide ion is the same for each of the three halide ions studied. This is considerably different from the interactions in aqueous solution.

Introduction

The behavior of silver ions in molten nitrates has been studied by several investigators. Laity measured activity coefficients in the silver–sodium nitrate system in concentration cells with transference.[3] Flengas and Rideal, in a classic study, demonstrated that the silver electrode behaved ideally,[4] and using a concentration cell they carried out electrometric titrations of silver ions with various halides in 1:1 $NaNO_3$–KNO_3 melts. Blander, *et al.*, measured the e.m.f. of cells containing $AgNO_3$ and KCl in molten KNO_3 and NaCl in molten $NaNO_3$.[5,6] In a previous report the present authors have shown that a reference electrode consisting of a mercury filled glass bulb functioned very well in Li–K nitrate eutectic.[7] The potential of the glass reference electrode differs for different electrodes, but in the case of potentiometric titrations one is interested only in differences rather than absolute values. The object of the present study was to investigate the behavior of silver(I) halides in Li–K nitrate eutectic *via* electrochemical techniques employing the glass reference electrode.

Experimental

All chemicals used, except the $AgNO_3$, were reagent grade and were used directly without further purification other than oven drying at 120°. The silver nitrate was also reagent grade but only hand-picked clear crystals were used in the investigation. Silver wire was B & S gage 18 of 99.99% purity. All nitrogen used was of extra-dry quality.

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[1] Part of the work submitted by H. Ti Tien to Temple University in partial fulfillment of requirements for degree of Doctor of Philosophy.

[2] Author to whom all inquiries should be sent.

[3] R. W. Laity, *J. Am. Chem. Soc.*, **79**, 1849 (1957).

[4] S. N. Flengas and E. K. Rideal, *Proc. Roy. Soc.* (London), **A233**, 443 (1956).

[5] M. Blander, F. F. Blankenship, and R. F. Newton, *J. Phys. Chem.*, **63**, 1259 (1959).

[6] M. Blander and J. Braunstein, *Ann. N. Y. Acad. Sci.*, **79**, 838 (1960).

[7] G. W. Harrington and H. T. Tien, *J. Phys. Chem.*, **66**, 173 (1962).

The electrolytic cell, furnace arrangement, and measuring and recording circuit were as described previously[7] with two changes. In this work temperature was controlled by a mercury-to-mercury thermoregulator which held temperature to within ±0.1°. The second modification was in the bottom of the furnace cavity. It was changed so that a 40-watt elongated light bulb could be inserted. This illumination, through the melt, permitted constant visual observation.

The reference electrode was as described previously[7] with the following modification. The tungsten wire used to establish electrical contact in the bulb was sealed into the stem under vacuum to prevent any possibility of oxidation or contamination. The silver electrode was constructed by sealing a length of silver wire into a capillary of soft glass. It was polished with fine emery cloth and then treated with 1:1 nitric acid containing a small amount of $NaNO_2$ before using in the melt as suggested by Clark.[8]

Procedure.—The filtered eutectic solvent (usually 250 g.) was placed in the cell and the temperature was raised gradually. Once melted (at about 132°) extra dry nitrogen was bubbled through the melt continuously throughout the rest of the run. The run usually began after the melt had reached and maintained the desired temperature for 3 hr. By this time the voltage between the reference electrode and the silver electrode did not change more than 1 mv./hr. Using usual notation, the cell may be represented as

$$\mathrm{Ag}\left|\begin{array}{c}\text{Li–K nitrate eutectic}\\ \mathrm{AgNO_3 + KX}\end{array}\right\vdots\begin{array}{c}\text{glass elec-}\\ \text{trode}\end{array}$$

The applicability of the Nernst equation to the cell was first investigated as follows. Increments of pulverized silver nitrate, weighed to within 0.1 mg., were added to the melt and the e.m.f. was measured for each addition after thermal equilibrium was re-established. Plots of e.m.f. *vs.* log $[Ag^+]$ were linear, having slopes predicted by the Nernst equation. In a typical run, at 211.5°, the experimental slope was 96.1 mv. and the predicted slope was 96.2 mv.

The precipitation reactions then were conducted. The e.m.f. was measured after each addition of KCl, KBr, and KI, as the case might be. The response of the silver electrode was immediate. The voltage readings were stable practically immediately.

The effect of temperature on the solubilities of AgCl, AgBr, and AgI were carried out in an identical manner to that described above. Measurements were made at 148.5, 172.0, 194.5, and 211.5°.

Treatment of Data

The evaluation of solubility products of silver halides in aqueous solutions has been well worked out.[9] A similar method was used in the present study. In the following, a brief outline is given to illustrate the method employed. Let C_{Ag} be the initial concentration of $AgNO_3$, C_{Cl} represent the KCl which had been added at any instant, and [Ag] and [Cl] represent the equilibrium concentrations of each of these ions. At any time during the reaction after the melt has been saturated with AgX (where X = Cl, Br, or I) the silver ion concentration may be calculated from the measured e.m.f. by the Nernst equation, in its usual form

$$E = E' - (RT/F) \ln [Ag^+] \qquad (1)$$

E' does not have to be evaluated since the silver ion concentration at any instant is determined from knowledge of the initial concentration and the change in e.m.f. The concentration of chloride is then given by

$$[Cl^-] = C_{Cl} - C_{Ag} + [Ag^+]$$

The solubility product, K_{sp}, is then equal to $[Ag^+] \times [Cl^-]$. This calculation assumes that the halide ion remains in solution as X^- and not in any complexed form such as AgX_2^-. This assumption appears to be justified by the experimental results. Examination of the sample data presented in Table I shows the constancy of the solubility product for a wide variety of Ag^+ and X^- concentrations. If complexing occurred, it would be expected that the K_{sp} calculated by this method would vary with concentration. Ion pair formation, such as $Ag^+–X^-$, might occur but that would not affect the value of K_{sp} when determined by the present method. The solubility product would have to be determined by a different experimental method to take into account any ion pair formation. Direct solubility measurements, for example, might give somewhat higher values.

Table I[10]

Ion fraction			
$Ag^+ \times 10^6$	$Cl^- \times 10^4$	T, °C.	$K_{sp} \times 10^{10}$
1.20	3.68	148.0	4.43 ± 0.04
0.815	5.51		4.49
.571	7.92		4.52
.447	9.98		4.46
6.60	2.10	172.0	13.9 ± 0.4
1.66	8.14		13.5
0.894	15.8		14.1
10.7	4.19	194.5	45.0
6.56	6.90		45.3
4.76	9.47		45.1
2.50	37.1	211.5	92.7
1.70	54.0		91.8
1.33	69.5		92.4
$Ag^+ \times 10^8$	$Br^- \times 10^4$		
2.07	1.74	148.0	0.0360 ± 0.0004
0.922	3.85		.0355
.626	5.77		.0361
5.48	2.08	172.0	.114 ± 0.004
5.06	2.33		.118
3.34	3.59		.120
124.	0.317	194.5	.394
67.4	.580		.391
39.1	1.04		.407
33.8	1.72	211.5	.581
22.0	2.63		.579
16.9	3.63		.613
$Ag^+ \times 10^6$	$I^- \times 10^4$		
0.158	0.804	148.0	0.000126 ± 0.000004
.0688	1.80		.000124
.0235	5.53		.000130
1.10	0.725	172.0	.000799
0.378	2.11		.000798
.155	5.17		.000800
1.11	3.19	194.5	.00353 ± 0.00004
0.626	5.77		.00361
.430	8.31		.00357

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[8] W. M. Clark, *J. Chem. Soc.*, 749 (1928).

[9] I. M. Kolthoff, "Volumetric Analysis, I" translated by N. H. Furman, John Wiley and Sons, Inc., New York, N. Y., 1928, Chapters 1–3.

[10] Supplementary data have been deposited as Document Number 7389 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

TABLE II

	AgCl		AgBr		AgI	
Temp.	$-\log K_{sp}{}^{d}$	$N \times 10^5$	$-\log K_{sp}$	$N^e \times 10^6$	$-\log K_{sp}$	$N \times 10^7$
25.0[a]	13.23	0.0241	15.7	0.0127	19.5	0.00163
148.5[b]	9.34	2.11	11.4	1.88	13.8	1.13
172.0[b]	8.84	3.77	10.9	3.40	13.1	2.82
172.0[c]	9.74	1.34	10.6	4.52	12.3	6.39
194.5[b]	8.34	6.70	10.3	6.40	12.4	5.96
211.5[b]	8.03	9.61	10.2	7.59	...	...

[a] Water, ref. 10. [b] In molten nitrate. [c] Water, extrapolated value (see text). [d] K_{sp} = solubility product in terms of mole fraction. [e] N = mole fraction AgX.

Table II presents average values at each temperature and additional data which will be discussed below.

Since the solubility product is an equilibrium constant, it is related to the free energy change by the familiar equation

$$K_{sp} = \exp(-\Delta F^0/RT) \qquad (2)$$

Hence, using the well established equations of thermodynamics ΔH^0 and ΔS^0 of the solution may be calculated. The two other equations involved are

$$\Delta F^0 = \Delta H^0 - T\Delta S^0 \qquad (3)$$

and

$$\mathrm{d} \ln K_{sp}/\mathrm{d}T = \Delta H^0/RT^2 \qquad (4)$$

Assuming ΔH^0 is independent of temperature, eq. 4 may be integrated to give

$$\log K_{sp} = \Delta H^0/2.303T + C' \qquad (5)$$

where C' is the integration constant. A plot of $\log K_{sp}$ *vs.* $1/T$ will be linear if ΔH^0 is independent of temperature as assumed. ΔH^0 then may be calculated from the slope of the line. For the temperature ranges investigated, all such plots were linear, indicating that the heats of solution are constant over this range. For the three halides investigated, the equations are

$$\log K_{sp}^{AgCl} = -9814/T + 1.667 \qquad (6)$$

$$\log K_{sp}^{AgBr} = -11680/T + 1.042 \qquad (7)$$

$$\log K_{sp}^{AgI} = -14290/T + 2.432 \qquad (8)$$

TABLE III

THERMODYNAMIC QUANTITIES FOR THE REACTION

$Ag^+ + X^- \rightleftharpoons AgX$

	ΔF^0, cal./mole	ΔH^0, cal./mole	ΔS^0, e.u.
	AgCl		
H_2O (25°)	13,295	15,650	7.90
Melt (172°)	18,000	19,500	4.0
H_2O (172°)	(12,750)	(15,650)	(6.0)
	AgBr		
H_2O (25°)	16,778	20,150	11.30
Melt (172°)	22,300	23,200	2.0
H_2O (172°)	(14,660)	(20,150)	(12.0)
	AgI		
H_2O (25°)	21,930	26,470	15.22
Melt (172°)	26,700	28,400	4.0
H_2O (172°)	(18,120)	(26,470)	(19.0)

The calculated values of ΔF^0, ΔH^0, and ΔS^0 are given in Table III. The figures in parentheses are extrapolated and will be discussed later.

Discussion

There are several interesting observations that can be made as a result of this investigation. Among the more significant are those that come from comparing the silver halide solubilities in molten nitrates to those in water. As can be seen in Table II, the relative solubilities are in the same order in the molten solvent as they are in water, *i.e.*, $Cl^- > Br^- > I^-$. The magnitudes of the solubilities are, of course, difficult to compare because of temperature differences. Aqueous solubility data are available, however, over a range of temperatures.[11,12] When $\log K_{sp}$ for aqueous solutions is plotted *vs.* $1/T$, a very straight line is obtained which may be extrapolated to obtain values for a hypothetical solution at 172°. The data are shown in Table II. As may be seen, the solubilities at 172° in the melt and in water are very close. In fact, the bromide and iodide are more soluble in water at this temperature.

Since the solubilities are similar, the standard free energies will be similar. That this is the case may be seen from the data in Table III. It will be noted, however, that the entropy terms are quite different. It is only when one considers this term that the true difference between the solvents becomes apparent.

According to Gurney[13] the center of interest in a dilute solution lies in the region of solvent immediately surrounding the solute ion. He terms this region the co-sphere of the ion or simply the co-sphere. When any pair of ions is introduced into a solvent, there will be a change of entropy in the co-sphere of each ion. The co-sphere of each species will depend on the charge, size, and perhaps the electronic structure of the ion. If one knew the value of this change for the ions Ag^+ and Cl^- and likewise for the ions Ag^+ and Br^-, any difference between the quantities could be associated with the differences in the co-spheres of the halides since the effect of Ag^+ would not be very different in the two cases.

In order to evaluate the entropy change of the co-sphere, Gurney separates the entropy change into two parts, a unitary part and a cratic part. The former refers to the part which is characteristic of the process and the latter depends on the amount of solvent as well as the amount of solute. Following the method outlined by Gurney,[12] the cratic and unitary entropy terms were calculated for the aqueous solutions at 25° and the molten solutions at 172°.

For dilute solutions the cratic term is given by $2R \ln N$, where N is mole fraction of solute. The unitary term then is the difference between the partial molal en-

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(11) B. B. Owen and S. R. Brinkley, *J. Am. Chem. Soc.*, **60**, 2233 (1938).

(12) "Handbook of Chemistry and Physics," 35th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1953–1954, p. 1634.

(13) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., Inc., New York, N. Y., 1953, pp. 4, 90–97, 178–181.

tropy and the cratic entropy.[14] The data are presented in Table IV.

Table IV

	AgCl		AgBr		AgI	
	H_2O (25°)	melt (172°)	H_2O (25°)	melt (172°)	H_2O (25°)	melt (172°)
Entropy of crystal	23.0	28.9	25.6	31.2	27.1	33.0
Entropy of solution	52.5	43.8	67.6	51.7	88.8	62.9
Partial molal entropy	75.5	72.7	93.2	82.9	115.9	95.9
Cratic entropy	60.6	40.5	72.3	50.0	89.6	59.9
Difference in unitary entropy	...	...	6.0	0	11.4	4

The last item in Table III is the difference between the unitary entropy of AgCl and each of the other halides. As is evident from these data, there is in water a progressive increase in entropy associated with the halide ion and its co-sphere. This increase is of the form $Cl^- < Br^- < I^-$. In molten Li–K nitrate eutectic, however, the difference between Cl^- and Br^- is essentially zero and between Cl^- and I^- only 4 e.u. This may be interpreted to mean that the three halides behave quite alike in the nitrate melt, whereas they exhibit great differences in an aqueous solution.

These results are not unexpected since water is a polar solvent and the molten nitrate is completely ionic. It is interesting, however, that the ion–ion interaction in the nitrate melt is essentially the same regardless of which halide is present. This may be associated, in part at least, with the low polarizability of the nitrate ion.

One may pursue this comparison still further by comparing the standard unitary entropies for each of the solvents at the same temperatures. The values of ΔS^0 are presented in Table III. The values for H_2O at this temperature were calculated from extrapolated data as mentioned above. Standard cratic entropies were calculated according to the method of Gurney.[12] The values of 10 and 16 e.u. were obtained for the Li–K nitrate eutectic and water solutions, respectively, at 172°. The standard unitary entropies are presented in Table V.

Table V

Standard Unitary Entropy of Solution, e.u.

Li–K nitrate eutectic (172°)			Aqueous solution (172°)		
AgCl	AgBr	AgI	AgCl	AgBr	AgI
−6	−8	−6	−10	−4	+3

It is interesting to note that the unitary part of the standard entropy increases with the size of the anion in aqueous solution but shows almost no variation in the molten nitrate solvent. The negative entropies in Table V signify an increase of order in the co-spheres; hence, in water, at this temperature, the chloride ion has the most ordered co-sphere. In the molten solvent, the differences between each of the anions is so small that one cannot say which anion exerts the greatest influence on the solvent molecules in its vicinity. These conclusions are in agreement with those discussed above.

It seems apparent, from this investigation, that when chloride, bromide, or iodide ions are present in very low concentrations in molten Li–K nitrate eutectic, each of these ions behaves in essentially the same fashion with respect to the solvating anions. That this is the case is very apparent when the molten solution is contrasted to analogous aqueous solutions. While not completely unexpected, it is still somewhat surprising in view of the large differences in size and polarizabilities among the three halide ions. These factors apparently are only important in their influence on the over-all solvation as evidenced by the variation in solubility.

(14) In the interest of space the details of the calculation are not given since they are extensively covered by Gurney, ref. 13.

Contribution from the Chemical Physics Research Laboratory,
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The Vibrational Spectra and Structure of the Vanadyl Ion in Aqueous Solution

By J. C. Evans

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It is concluded from a study of the Raman and infrared spectra of aqueous solutions of vanadyl salts that, in solutions of the chloride, fluoride, and perchlorate, the vanadyl ion has the structure $[OV(OH_2)_n]^{+2}$ where n is not determined. In vanadyl sulfate solutions, association between the vanadyl and sulfate ion occurs, the sulfate ions replacing one or more of the water molecules in the vanadium coördination sphere.

Introduction

Early oxidation–reduction potential studies of the V^{+4}–V^{+5} system were interpreted in terms of the structures VO^{+2} for the vanadyl ion and VO_2^+ for the pervanadyl ion.[1] Later, Rossotti and Rossotti[2] concluded from spectrophotometric (electronic spectra) and from potentiometric measurements on vanadyl perchlorate solutions that the predominant ionic species is either

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(1) A. B. Hart and J. R. Partington, *J. Chem. Soc.*, 1532 (1940).

(2) F. J. C. Rossotti and H. Rossotti, *Acta Chem. Scand.*, **9**, 1177 (1955).