respect to each other leads to $M^{x+}Mo_8O_{30}^{(12-x)-}$ (Figure 4), examples of which are not known. Loss of six metal atoms approximately octahedrally placed leads to $M^{x-}Mo_6O_{24}^{(12-x)-}$ (Figure 4), which is the structure found for the 1:6 heteropolymolybdates listed above.

The formation of large heteropolyanions of this type would be expected to be less favorable with the larger tungsten(VI) atoms, which appears to be in agreement with observation.

Group III.—The structure of $Ce^{IV}Mo_{12}O_{42}^{8-}$ is based on an icosahedrally coordinated cerium atom surrounded by six pairs of face-sharing octahedra.[14] Such face sharing of octahedra produces severe Coulombic interactions, and it is therefore not unexpected that tungsten forms only the 1:8 heteropolyanion $Ce^{IV}W_8O_{28}^{4-}$.[15]

(14) D. D. Dexter and J. V. Silverton, *J. Am. Chem. Soc.*, **90**, 3589 (1968).
(15) R. Ripan and I. Todorut, *Roczniki Chem.*, **38**, 1587 (1964); *Rev. Roumaine Chim.*, **11**, 1279 (1966).

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Association and Hydration Equilibria in NH_4NO_3–$2H_2O$–(AgCl or AgBr)[1]

Recently, from his measurements of the solubilization of silver chloride by excess chloride and of silver bromide by excess bromide in the solvent NH_4NO_3–$2H_2O$, Gal reported association constants for the formation of the associated species AgCl, $AgCl_2^-$, AgBr, and $AgBr_2^-$.[2] Application of the equations of a quasilattice model of anhydrous molten salts[3a] to the "pseudomolten salt" NH_4NO_3–$2H_2O$[3b] seemed to indicate nonlinear rather than linear $AgCl_2^-$ species. Although the absence of data in anhydrous NH_4NO_3 prevents a complete interpretation in terms of a recent aqueous quasilattice model of competition between association and hydration equilibria, it is of interest, nevertheless, to discuss Gal's results in this context.[4]

According to the aqueous quasilattice model, the measured pairwise association constants, K_1 (for AgCl or AgBr), should depend on water content as

$$Z/K_1 = \exp[\epsilon_C/kT] + R_H \exp[(\epsilon_C - \epsilon_H)/kT] \quad (1)$$

where Z is the lattice coordination number (usually assumed to be 6), ϵ_C is the relative silver–halide interaction energy for the exchange $Ag^+NO_3^- + NH_4^+X^- \rightleftharpoons Ag^+X^- + NH_4^+NO_3^-$ in anhydrous molten salt, ϵ_H is the relative hydration energy for $Ag^+NO_3^- + NH_4^+(H_2O) \rightleftharpoons Ag^+(H_2O) + NH_4^+NO_3^-$, R_H is the water concentration expressed as the mole ratio, moles of water per mole of nitrate, k is the Boltzmann constant, and T is the absolute temperature.[4] With eq 1, setting $Z = 6$, it is possible to obtain ϵ_C and ϵ_H from data at two different temperatures although, since ϵ_C is generally of much larger magnitude than ϵ_H, the numerical evaluation of the parameters is imprecise without data for the anhydrous solvent. The model assumes that the hydration energy parameter ϵ_H is the same for the AgCl and AgBr systems. In order to test this, we have inferred reasonable values of ϵ_C for the AgCl and AgBr associations in anhydrous NH_4NO_3 from known values of association energies in molten alkali nitrates.

We also have recalculated the pair equilibrium constants for AgCl and AgBr by graphical extrapolation, since the curve-fitted values often tend to weight the high-concentration data where higher species such as $AgCl_2^-$ or $AgBr_2^-$ predominate.[5] Values of

$$K_1 = \lim_{m_x \to 0} [\partial \ln (Sm_x/\mathrm{KSP})/\partial m_x] = \lim_{m_x \to 0} \{\partial[(Sm_x/\mathrm{KSP}) - 1]/\partial m_x\}$$

were obtained from plots of ln (Sm_x/KSP) and of $[(Sm_x/\mathrm{KSP}) - 1]$ *vs.* m_x for the low concentration data, as in Figure 1. Both plots have the same limiting slope, but at finite concentrations the logarithmic plot is concave downward and the rational plot is concave upward, so that upper and lower limits to the association constant can be estimated. S is the solubility, m_x the molality of ligand, and KSP the solubility product, which was found by successive approximations. It is seen in Figure 2 that the plots of log K_1 *vs.* $1/T$ and of log KSP *vs.* $1/T$ are smoother for the graphically estimated values than for those reported by Gal. These recalculated values in Table I were used in subsequent calculations, although little difference would have resulted from using Gal's values. The values of K in parentheses refer to concentrations expressed as mole ratios (R_x moles of ligand per mole of solvent); all others refer to conventional molality units (in moles of ligand per kilogram of solvent)).

In the absence of measured values of $K_{AgCl(AgBr)}$ or of ϵ_C for AgCl or AgBr (*i.e.*, $\epsilon_{AgCl(AgBr)}$) in anhydrous NH_4NO_3, it seems reasonable to estimate values from association equilibria in molten alkali nitrates.[6] Because the nitrate ion is closer in size to the bromide ion than to the chloride ion, the solvent cation size affects the electrostatic part of the silver–bromide association less than that of the silver–chloride association, and ϵ_{AgBr} is therefore subject to less uncertainty than ϵ_{AgCl} in estimating the parameters in NH_4NO_3. In dilute aqueous solution at 25° K^+ and NH_4^+ have the same effective radii and mobilities, and their chlorides have nearly identical activity coefficients.[7] However, at elevated temperatures and high salt concentrations, water

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corp.
(2) I. J. Gal, *Inorg. Chem.*, **7**, 1611 (1968).
(3) (a) M. Blander, *J. Chem. Phys.*, **34**, 432 (1961); (b) J. M. C. Hess, J. Braunstein, and H. Braunstein, *J. Inorg. Nucl. Chem.*, **26**, 811 (1964).
(4) J. Braunstein, *J. Phys. Chem.*, **71**, 3402 (1967).
(5) J. Braunstein, M. Blander, and R. M. Lindgren, *J. Am. Chem. Soc.*, **84**, 1529 (1962).
(6) M. Blander, "Molten Salt Chemistry," Interscience Publishers, New York, N. Y., 1964, p 228.
(7) B. F. Wishaw and R. H. Stokes, *Trans. Faraday Soc.*, **49**, 27 (1953).

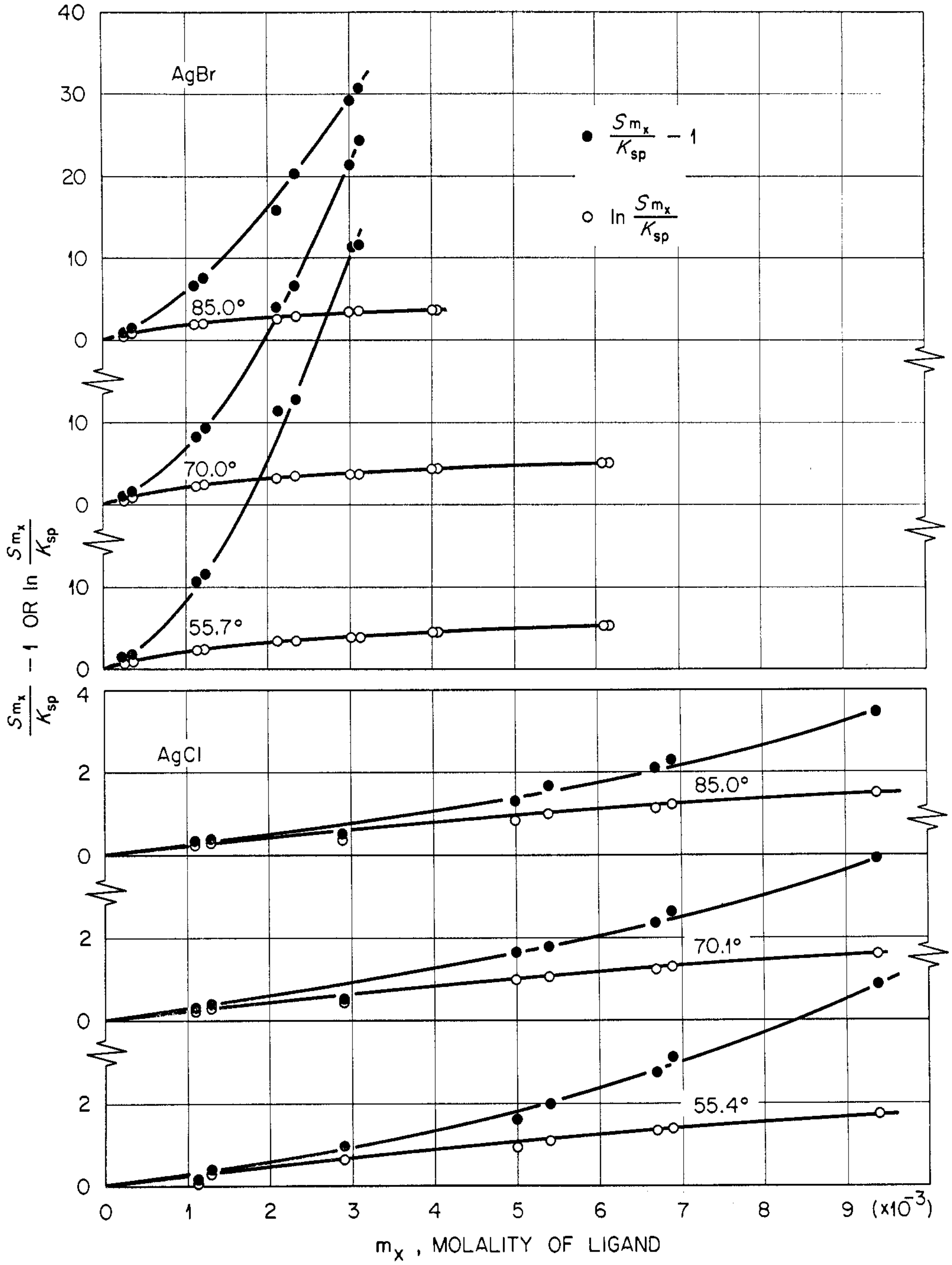

Figure 1.—Graphical extrapolation to obtain the association constants K_1(AgCl) and K_1(AgBr) in NH_4NO_3–$2H_2O$ from the solubility data of Gal at low concentrations of excess chloride and excess bromide.

TABLE I

RECALCULATED VALUES OF K_{AgCl}, K_{AgBr}, KSP_{AgCl}, AND KSP_{AgBr} IN NH_4NO_3–$2H_2O$

Temp, °C	K_{AgCl}, *m* (mole ratio)	K_{AgBr}, *m* (mole ratio)	KSP_{AgCl}, *m*	KSP_{AgBr}, *m*
55	260 (2240)	4970 (4.27×10^4)	1.12×10^{-8}	5.0×10^{-11}
70	240 (2065)	3840 (3.31×10^4)	2.51×10^{-8}	1.00×10^{-10}
85	220 (1890)	3330 (2.88×10^4)	5.01×10^{-8}	2.51×10^{-10}

activities in ammonium nitrate[8] are closer to values in sodium nitrate[9] than in potassium nitrate.[9] Thus, molten sodium nitrate may be a better analog of ammonium nitrate than potassium nitrate. Within the framework of the aqueous model, this is borne out by the fact that, applying eq 1 at all three temperatures, the calculated difference $RT \ln (K_{AgCl}/K_{AgBr}) = \epsilon_{AgBr} - \epsilon_{AgCl} = -1.9$ kcal/mol in ammonium nitrate is closer to that difference in sodium nitrate (−1.64 kcal/mol) than to that in potassium nitrate (−1.23 kcal/mol). Assuming $\epsilon_{AgBr[NH_4NO_3]} \cong \epsilon_{AgBr[NaNO_3]} =$

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(8) A. N. Campbell, J. B. Fishman, G. Rutherford, T. P. Schaefer, and L. Ross, *Can. J. Chem.*, **34**, 151 (1956).

(9) L. P. Shpigel and K. P. Mishchenko, *J. Appl. Chem. USSR*, **40**, 659 (1967).

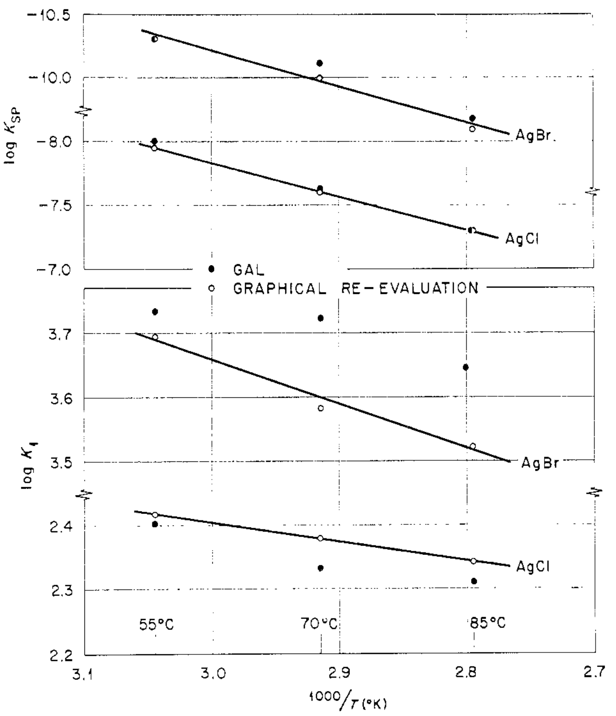

Figure 2.—Logarithms of association constants K_1(AgCl) and K_1(AgBr) and of solubility product constants KSP(AgCl) and KSP(AgBr) in NH_4NO_3-$2H_2O$ *vs.* reciprocal temperature (°K): ●, values reported by Gal; ○, values recalculated by graphical extrapolation.

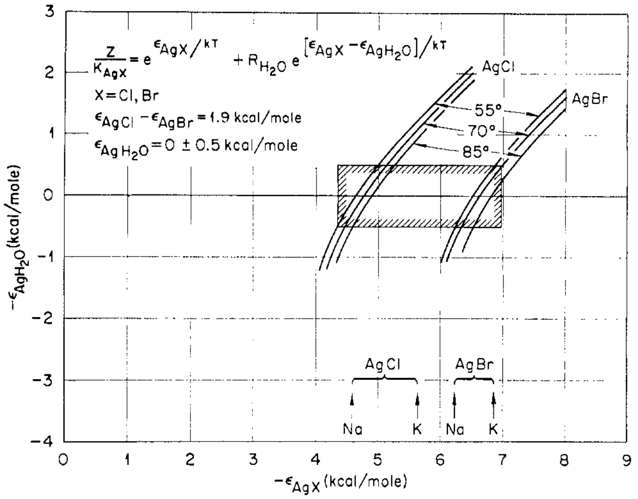

Figure 3.—Comparison of the aqueous quasilattice model with Gal's solubilities in the systems NH_4NO_3–$2H_2O$–(AgCl or AgBr). Values of ϵ_{AgH_2O} consistent with both the experimental measurements and the model equation and corresponding to values of ϵ_{AgCl} and ϵ_{AgBr} for the anhydrous system.

−6.3 kcal/mol leads to the estimated values $\epsilon_{AgCl[NH_4NO_3]} = -4.4$ kcal/mol and ϵ_H $(= \epsilon_{AgH_2O[NH_4NO_3]})$ = 0 ± 0.5 kcal mol. The last value, while uncertain, is not unreasonable in its range of values.

A crude estimate of $\epsilon_{AgH_2O} = +0.7$ kcal/mol[10] can be obtained from the stability constants of silver–ammine complexes in aqueous ammonium nitrate solutions,[11] albeit at water contents above the range of the model. The heats of vaporization of water from concentrated aqueous silver nitrate solutions and from concentrated aqueous ammonium nitrate solutions differ by less than 0.1 kcal/mol,[8] suggesting a value near zero for ϵ_{AgH_2O}.

Hess has noted slightly greater stability of $CdCl^+$ in $NaNO_3$–$6H_2O$ than in NH_4NO_3–$6H_2O$, 0.13 kcal/mol, again suggesting that NH_4^+ has a smaller effective radius in concentrated solutions at high temperatures than in water at 25°.[12] This change in behavior may not be surprising. In dilute solutions at low temperatures the effective size and mobility of NH_4^+ are related to the way in which its protons take part in the hydrogen-bonded water structure while at higher salt concentrations and temperatures extensive hydrogen-bonded structure cannot persist.

Figure 3 is a plot of mutually consistent values of ϵ_H and ϵ_C (chloride or bromide) calculated for each of Gal's six sets of measurements (chloride and bromide at three different temperatures each) with eq 1. If the model fit exactly, the curves for the three temperatures in each system would coincide. Their spread is about 0.2–0.45 kcal/mol. The arrows on the abscissa are values of ϵ_{AgCl} and ϵ_{AgBr} in molten $NaNO_3$ or KNO_3. Although a unique fit of the aqueous data by values of ϵ_{AgH_2O}, ϵ_{AgCl}, and ϵ_{AgBr} is not possible, the hatched rectangle indicates the range of values suggested by comparing the aqueous results with those obtained in anhydrous alkali nitrates; thus, $\epsilon_{AgH_2O} = 0 \pm 0.5$ kcal/mol, which corresponds to a nearly random distribution of water between silver ions and ammonium ions.

In its present stage, as a first approximation, the aqueous quasilattice model neglects anion hydration (*i.e.*, water on cation sites and hence water–anion contacts) which may be significant.[13–15] An extension of the model, in progress, will permit occupancy of cation sites (as well as anion sites) by water molecules.

Additional experiments in this system would be of considerable interest for testing the aqueous quasilattice model. This model provides a useful framework for representing competing equilibria in very concentrated electrolyte solutions for which no other workable model has been proposed.

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(10) J. Braunstein, *Inorg. Chim. Acta Rev.*, **2**, 19 (1968).

(11) J. Bjerrum, "Metal Ammine Formation in Aqueous Solutions," P. Haase and Sons, Copenhagen, 1957, p 134.

(12) J. M. C. Hess, Ph.D. Dissertation, University of Maine, 1961, p 96; University Microfilms, Ann Arbor, Mich., No. 61-5210.

(13) D. E. Irish and A. R. Davis, *Can. J. Chem.*, **46**, 943 (1968).

(14) A. G. Keenan, *J. Phys. Chem.*, **61**, 780 (1957).

(15) P. Kebarle, M. Arshadi, and J. Scarborough, *J. Chem. Phys.*, **49**, 817 (1968).

(16) Oak Ridge Graduate Fellow from the University of Maine under appointment from Oak Ridge Associated Universities.