

Yada, Tanaka and Nagakura⁹ obtained for amine-iodine complexes the relationship

$$+ \Delta H^0 = -1.667 + 0.545\Delta S^0 \quad (11)$$

The slopes of the two straight lines are essentially identical. This result is perhaps to be expected from the analysis given earlier¹⁰ of the relationship between ΔH and ΔS for amine complexes. Certainly, if the argument given there concerning the slope of the ΔS vs. ΔH plot is correct, the same argument should apply to the plot for the nitrile-IX complexes, since a weak N-I bond is involved in both cases.

Since a linear relationship between ΔS and ΔH for these complexes is apparently found, one of the conditions necessary for a successful linear correlation between $\log K$ and σ^* is fulfilled, in agreement with the empirical finding (Fig. 1). Since

$$\Delta(\Delta F) = 2.3RT\rho^*\sigma^* = \Delta(\Delta H) - T\Delta(\Delta S)$$

and since, from equation 9

$$\Delta(\Delta S) = 1.85\Delta(\Delta H)$$

it follows that

$$\Delta(\Delta H) = \frac{2.3 \times 2.0T\rho^*\sigma^*}{1000} / 1 - \frac{1.85T}{1000}$$

$$\Delta(\Delta H) = 2.5\rho^*\sigma^*$$

at 300° K. Thus, a plot of ΔH vs. σ^* should give a line with greater slope than the corresponding plot of $\log K$. However, when we attempt this plot using our data,

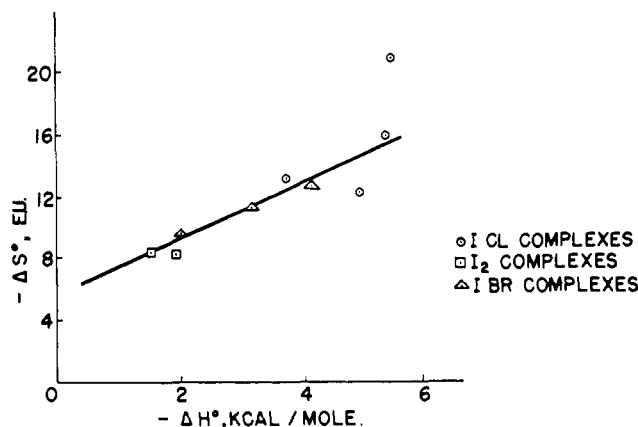


Fig. 2.—Relationship between entropies and enthalpies of formation for nitrile-halogen complexes.

we find considerable scatter, due to the unavoidably large error in the determination of ΔH . Thus, in our case, we find the correlation of $\log K$ with σ^* to be more successful than the correlation of ΔH vs. σ^* .

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Heats of Solution of Solids in Molten Reciprocal Salt Systems

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The heat of solution of solid AgCl in molten KNO₃, calculated from solubility and e.m.f. measurements by rigorous thermodynamic methods, is 19.2 ± 0.6 kcal/mole. This value is in excellent agreement with a value of 19.6 ± 1.0 kcal/mole estimated from a cycle first proposed by Flood, Förland and Grjotheim illustrating the usefulness of this cycle in making predictions *a priori*.

In accordance with the considerations of Flood, Förland and Grjotheim,³ the heat of solution of a solid such as AgCl in a solvent such as KNO₃ may be estimated from a knowledge of the heat changes for the three processes

- (A) $\text{AgCl(sol.)} + \text{KNO}_3(\text{liq.}) \longrightarrow \text{AgNO}_3(\text{liq.}) + \text{KCl(liq.)} \Delta H_A$
- (B) $\text{AgNO}_3(\text{liq.}) \longrightarrow \text{AgNO}_3(\text{infinite diln. in KNO}_3) \Delta H_B$
- (C) $\text{KCl(liq.)} \longrightarrow \text{KCl(infinite diln. in KNO}_3) \Delta H_C$

with processes of the first type usually leading to the largest contribution to the total heat (or excess free energy) of solution in reciprocal systems. This method of estimation of heats of solution in reciprocal molten salt systems is operationally more useful and sound than the Born cycle which has been used previously⁴ to rationalize heats of solution in a similar system but which cycle could not be used for a prediction *a priori*.

This study was undertaken to obtain, for comparison with the above prediction, a reliable value for the heat of solution of solid AgCl in molten KNO₃ which was calculated so as to take into account the known non-ideal behavior of the solution.⁵⁻⁷ None of the previously reported heats of solution^{4,3,9} in similar systems were corrected specifically for non-ideal behavior and hence are invalid, and the apparent heats of solution can only be correct by a fortuitous cancellation of factors.

The heat of solution may be calculated from the thermodynamic equation

$$\frac{d \ln (a_{\text{AgNO}_3} a_{\text{KCl}} / a_{\text{KNO}_3})}{d(1/T)} = \frac{H^\square - \bar{H}^*}{R} = - \frac{\Delta H_{\text{soln.}}}{R} \quad (1)$$

where the activities (a_i) are in solutions saturated with solid AgCl. If the standard states of AgNO₃ and

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(3) H. Flood, T. Förland and K. Grjotheim, *Z. anorg. u. allgem. Chem.*, **276**, 289 (1954).

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(6) J. Braunstein and M. Blander, *ibid.*, **64**, 10 (1960).

(7) D. L. Manning and M. Blander, *ibid.*, **66**, 2069 (1962).

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(9) J. Jordan, J. Meier, E. J. Billingham, Jr., and J. Pendergrast, *Nature*, **187**, 318 (1960); *Anal. Chem.*, **31**, 1439 (1959). It should be noted that the error in the heat of solution from these measurements probably is relatively small. As has been noted by these authors, the error in the solubility or activity products may be appreciable, and depends on details of the solution behavior which may not yet have been investigated.

KCl are chosen such that the activity coefficients are unity at infinite dilution of all solutes in KNO_3 then \bar{H}^* is the partial molar heat content of AgCl at infinite dilution; H^\square is the heat content of solid AgCl and ΔH_{soln} is the heat of solution of solid AgCl . To calculate the heat of solution one needs, $(d \ln a_{\text{AgNO}_3}/d(1/T))$, $(d \ln a_{\text{KCl}}/d(1/T))$, and $(d \ln a_{\text{KNO}_3}/d(1/T))$ in a saturated AgCl solution. In this paper, the first quantity is obtained directly from e.m.f. measurements and the second from measurements of the solubility of AgCl and a thermodynamic calculation of the activity coefficients of KCl from the activity coefficients of AgNO_3 by integrating the exact thermodynamic equation

$$\left(\frac{\partial \ln \gamma_{\text{AgNO}_3}}{\partial R_{\text{KCl}}}\right)_{R_{\text{AgNO}_3}} = \left(\frac{\partial \ln \gamma_{\text{KCl}}}{\partial R_{\text{AgNO}_3}}\right)_{R_{\text{KCl}}} \quad (2)$$

where R_i is the mole ratio (n_i/n_{KNO_3}) and n_i is the number of moles of component i . Since the solubility of AgCl is quite low, the last derivative, $(d \ln a_{\text{KNO}_3}/d(1/T))$, may be assumed to be zero.

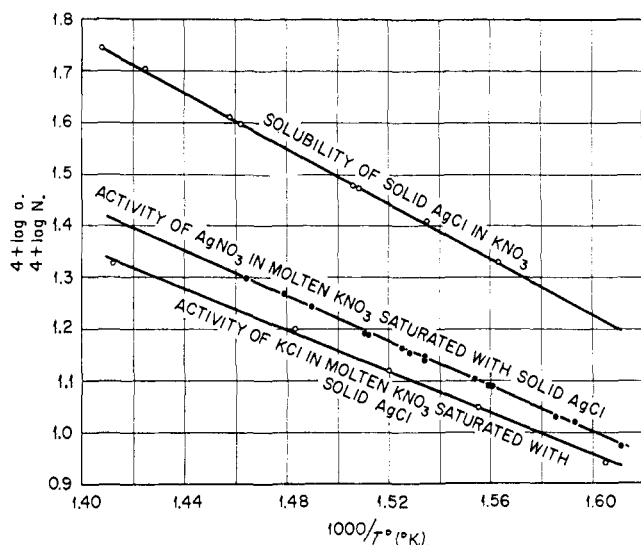


Fig. 1.—Solubilities and activities in molten KNO_3 .

The Activities of AgNO_3 and of KCl .—Using experimental techniques discussed previously^{5,6} the activities of AgNO_3 as a function of temperature were measured in the concentration cell



The materials, apparatus and procedure for the determination of a_{AgNO_3} in this cell were identical to those previously reported. Equimolar quantities of AgNO_3 and KCl were added to molten KNO_3 in the right-hand half-cell to form a saturated solution. The e.m.f. values for a typical series were measured over a period of 3.5 hours during which time the temperature was raised, lowered and raised again over the temperature interval within the range 350 – 440° . All but one of sixteen values of $\log a_{\text{AgNO}_3}$ obtained in one typical series, which is plotted in Fig. 1, fell on a single straight line within an error equivalent to less than 0.5 millivolt in the e.m.f. measurement. From Fig. 1 a value of -10.05 kcal./mole was calculated for $2.303R[d \log a_{\text{AgNO}_3}/d(1/T)]$. The smallest value derived was -9.95 and the largest -10.15 kcal./mole from several series of measurements.

The activity of KCl may be determined from a knowledge of the solubility of AgCl and a calculation of the activity coefficient of KCl at the concentration of Ag^+ and Cl^- ions at saturation. Visual measurements of the solubility of solid AgCl in molten KNO_3 were made over a large range of concentrations of Ag^+ and Cl^- ions in a one-liter tall form beaker set in a manually controlled resistance furnace of about 5 in. inside diameter. Solutions of AgNO_3 in about 500–600 g. of KNO_3 were flushed with pure helium and increments of KCl were added to the solution, which was vigorously stirred with a Pyrex propeller. After each increment of KCl , the solution was cooled at a rate of about 1° per minute. The temperature at which the first faint cloudiness appeared was taken as the liquidus temperature. Cooling the solution further by 0.5° yielded a pronounced precipitate. Seeding the solution with a AgCl crystal or by the use of a cold glass fiber yielded values of the liquidus temperature which were always within 0.5° of the value obtained without seeding. If the precipitate had not been allowed to agglomerate, the temperature at which all of the precipitate redissolved upon heating the melt was always within 0.5° of the measured liquidus. The temperature was controlled manually and was measured with a platinum vs. platinum-10% rhodium thermocouple set in a Pyrex well. The thermocouple was calibrated to $\pm 0.5^\circ$ against a thermocouple calibrated at the National Bureau of Standards. In Fig. 1 are plotted measured values of the solubility (mole fraction) of AgCl when equimolar quantities of AgNO_3 and KCl were in solution.

Previous measurements⁵⁻⁷ of the activity coefficients of AgNO_3 as a function of the concentration of KCl and AgNO_3 in unsaturated solutions were used to calculate (with a small extrapolation to saturated solutions) the activity coefficients of KCl . The integration of eq. 2 over the mole ratio of AgNO_3 (R_{AgNO_3}) leads to the relation

$$\log \gamma_{\text{KCl}}(R'_{\text{AgNO}_3} R'_{\text{KCl}}) = \int_0^{R'_{\text{AgNO}_3}} \left(\frac{\partial \log \gamma_{\text{AgNO}_3}}{\partial R_{\text{KCl}}}\right)_{R_{\text{AgNO}_3}} dR_{\text{AgNO}_3} \quad (3)$$

where the argument of the integral is evaluated at $R_{\text{KCl}} = R'_{\text{KCl}}$ and the reasonable assumption has been made that $\gamma_{\text{KCl}} = 1$ in dilute solutions of KCl containing no Ag^+ ions¹⁰; R'_{AgNO_3} and R'_{KCl} are concentrations in saturated solutions of AgCl and in this example are equal. A graphical evaluation of

$$\left(\frac{\partial \log \gamma_{\text{AgNO}_3}}{\partial R_{\text{KCl}}}\right)_{R_{\text{AgNO}_3}}$$

at R'_{KCl} was made from large scale plots of $\log \gamma_{\text{AgNO}_3}$ vs. R_{KCl} at several fixed concentrations of AgNO_3 at 350 ,¹¹ 370 , 385 , 402 and 436° . These derivatives were plotted as a function of AgNO_3 and integrated graphically to give the values of $\log \gamma_{\text{KCl}}$ in saturated solutions of AgCl (equimolar in AgNO_3 and KCl) given in Table I. These quantities are added to the logarithm of the solubilities of AgCl to obtain the values of $\log a_{\text{KCl}}$ listed in Table I and plotted in Fig. 1. (Note that the solubility of AgCl is essentially equal to the concentration of KCl in a dilute saturated equimolar solution of AgNO_3 and KCl .) The slope of the plot leads to a value of $2.303R(d \log a_{\text{KCl}}/d(1/T))$ equal to 9.15 kcal./mole. Values of $\log a_{\text{AgNO}_3}$ meas-

(10) J. Braunstein and R. M. Lindgren, *J. Am. Chem. Soc.*, **84**, 1534 (1962).

(11) At 350° several supplementary sets of measurements were made so as to have 12 sets at concentrations of AgNO_3 ranging from about 5×10^{-3} to 1.66×10^{-2} mole ratio.

ured here were independently checked by multiplying the solubility of AgCl (essentially equal to the concentration of AgNO₃ in a saturated equimolar solution) by γ_{AgNO_3} obtained by a short extrapolation of measurements of $\gamma_{\text{AgNO}_3}^{5-7}$ to the solute concentrations R'_{AgNO_3} and R'_{KCl} in a saturated equimolar solution. Values of $\log a_{\text{AgNO}_3}$ obtained thus are given in Table I and checked with the values plotted in Fig. 1 well within the errors in the measurements. For obtaining the slope, $(d \log a_{\text{AgNO}_3}/d(1/T))$, the values plotted in Fig. 1 are probably more reliable. It might be noted that the fact that $a_{\text{KCl}} < a_{\text{AgNO}_3}$ in equimolar solutions of AgNO₃ and KCl is at least partly related to the conclusion that the species AgCl₂⁻ is more stable than Ag₂Cl⁺ in this solvent.⁷

TABLE I
SOLUBILITIES AND ACTIVITIES IN MOLTEN KNO₃ SATURATED WITH SOLID AgCl

T, °C.	-log s	-log γ_{KCl}	-log a_{KCl}	-log a_{AgNO_3}	-log ($a_{\text{AgNO}_3} a_{\text{KCl}}$)
350	2.787	0.274	3.061	2.997	6.058
370	2.652	.300	2.952	2.910	5.862
385	2.559	.322	2.881	2.839	5.720
402	2.456	.345	2.801	2.748	5.549
436	2.264	.409	2.673	2.590	5.263

Discussion

The heat of solution calculated from the experimental data using eq. 1 is $(10.05 + 9.15) = 19.2$ kcal./mole with an estimated error of about 0.6 kcal./mole.

The heat of solution may be estimated theoretically from $(\Delta H_A + \Delta H_B + \Delta H_C)$. The heat change for the metathetical reaction A, ΔH_A , is calculated as 19.9 kcal./mole using the data in Table II and under the reasonable assumptions that the differences between the heat capacities of the reactants and the products and the variations of heats of fusion with temperature are small enough to be neglected. From the data of Kleppa,¹² the heat change for the dissolution process B is calculated as -303 cal./mole. Although the heat of solution of the hypothetical liquid KCl in KNO₃ is not available, an indication of the magnitude of the

(12) O. J. Kleppa, R. B. Clarke and L. S. Hersh, *J. Chem. Phys.*, **35**, 175 (1961).

heat of solution of such binary systems may be obtained from other thermodynamic measurements. The phase diagrams of the KNO₃-KCl¹³ and the NaNO₃-NaCl¹⁴ systems indicate an undetectable deviation from ideal solution behavior of the nitrate solvent at the liquidus temperature. This indicates that, for process C, the heat of solution, which usually parallels the excess free energies of solution, is probably small (less than 1 kcal./mole).

TABLE II
THERMODYNAMIC DATA FOR THE CALCULATION OF ΔH_A ^a

	Heat of formation of solid ΔH_{298} , (kcal./mole)	Heat of fusion ΔH_{Fusion} (kcal./mole)	Heat of transition ΔH_{TR} (kcal./mole)
AgNO ₃	-29.43	2.76	0.66
AgCl	-30.36	3.16	—
KNO ₃	-117.76	2.8	1.3
KCl	-104.175	6.1	—

^a F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," USNBS Circular 500, 1952.

Hence, within about 1 kcal./mole, $(\Delta H_A + \Delta H_B + \Delta H_C) = 19.6$ kcal./mole which, within the expected errors, is equal to the value of 19.2 kcal./mole obtained from the experimental measurements.

If the free energy values are available, the use of processes such as A, B, and C may be used to calculate theoretically the values of the activity product, $a_{\text{AgNO}_3} a_{\text{KCl}}$, listed in Table I, since at saturation

$$RT \ln a_{\text{AgNO}_3} a_{\text{KCl}} = -\Delta F_A - (\bar{F}^*_{\text{AgNO}_3} - F_{\text{AgNO}_3}^\circ) - (\bar{F}^*_{\text{KCl}} - F_{\text{KCl}}^\circ) = F^c_{\text{AgCl}} - \bar{F}^*_{\text{AgCl}}$$

The Born cycle is not useful for estimating the activity product or the heats of solution because operational values of dielectric constants in molten salts are not available and even if measurable or meaningful must be known to a very high accuracy to lead to results as reliable and precise as are obtainable from consideration of processes such as A, B and C.

(13) E. Kordes, W. Bergmann and W. Vogel, *Z. Elektrochem.*, **55**, 600 (1951).

(14) E. R. Van Artsdalen, *J. Tenn. Acad. Sci.*, **29**, 122 (1954).

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Recoil Tritium Reactions: Pressure-dependent Reactions with Cyclobutane¹

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Recoil tritium atoms react with cyclobutane in the presence of O₂ scavenger to form mainly labeled cyclobutane, ethylene and HT. In the pressure range 0.07 to 1 atmosphere, the sum of cyclo-C₄H₇T and C₂H₃T yields is constant, but the fraction of this sum found as cyclo-C₄H₇T rises smoothly from 47% to 60%. In the liquid phase, the cyclo-C₄H₇T/C₂H₃T ratio is 4.6. The observed pressure dependence demonstrates the formation in the initial hot reaction of cyclo-C₄H₇T with sufficient excitation energy to cause unimolecular decomposition to C₂H₃T. The trend with pressure indicates a broad distribution of excitation energies for cyclo-C₄H₇T with a median energy of approximately 5 e.v. The initial specific radioactivity of the cyclo-C₄H₇T per H atom is approximately the same as that of CH₃T and n-C₄H₉T from the respective alkanes in direct competition in the same system.

Introduction

The chemical reactions of high kinetic energy tritium atoms have been investigated with a variety of hydrocarbons in order to establish the general characteristics of these hot reactions.^{2,3} The study of reactions with

(1) This research was supported by A.E.C. Contract No. AT-(11)-407.

cyclopropane has been of special interest because of its known unimolecular isomerization to propylene, its

(2) M. Henschman, D. Urch and R. Wolfgang, "Chemical Effects of Nuclear Transformations," International Atomic Energy Agency, Vienna, 1961, Vol. 2, p. 83.

(3) F. S. Rowland, J. K. Lee, B. Musgrave and R. M. White, *ref. 2*, p. 67.