tus used but the comparative results are general. The dependence of ΔT on NaCl concentration in the ammonium nitrate melt was also investigated briefly and the 0.05 to 1 mole ratio was found to give the largest value for $\Delta T_{\max}$. This is probably also close to the solubility of NaCl in the melt.

TABLE I

DIFFERENTIAL THERMAL ANALYSIS OF AMMONIUM NITRATE DECOMPOSITION

Salts listed were added in mole ratio 0.05:1.

Salt added	T, °C.	ΔTmax, °C.
..	270	6
NaF	270	7
NaI	270	7
$(NH_4)_2SO_4$	270	12
NaBr	270	22
NaCl	225	50
NH_4Cl	225	~64
$(NH_4)_2Cr_2O_7$	182	247

The decrease in ΔT after the maximum is passed is due in large part to disappearance of the sample by decomposition. However, examination of the sample tube when the temperature had reached 300° showed in general the presence of a few drops of a clear melt refluxing gently up the sides. In another connection, a similar residue was refluxed at 400° in a vacuum for about 10 min. without noticeable increase in pressure. A quantitative microanalysis of this material showed it to be ammonium nitrate. These observations provide another illustration of the fact, noted by Friedman and Bigeleisen,[4] that pure, dry ammonium nitrate is relatively stable to thermal decomposition. Presumably, in the above instances the water and other impurities had been purged out by the initial partial decomposition.

Discussion.—The thermal decomposition of ammonium nitrate has been studied in some detail previously, the latest results being those of Friedman and Bigeleisen.[4] The major products of decomposition are N_2O and H_2O but some free nitrogen also is formed, the proportion becoming greater at higher temperatures, *e.g.*, about 2% at 260°. Chlorides accelerate the reaction and also increase the proportion of nitrogen in the products to the range 30–50%.[5]

The DTA results obtained in the present research show rather clearly that the thermal decomposition of ammonium nitrate is a complex reaction. As shown in Figs. 1 and 2 and in Table I, there is one reaction, presumably the N_2-producing one, which is strongly catalyzed by chloride ion and, when so catalyzed, has a very high exothermicity with a differential thermal peak at 225° in the present apparatus. A slight indication of this reaction occurring in pure ammonium nitrate is shown by the weak maximum at 245° in Fig. 1. The major reaction occurring in the decomposition of pure ammonium nitrate, presumably the N_2O-producing one, has a relatively low exothermicity and gives a differential thermal peak at 270° in the present apparatus. This reaction is moderately catalyzed by bromide and ammonium ions.

The height of the differential thermal peak ($\Delta T_{\max}$) is a measure of the exothermicity and rate of the reaction while the location of the peak along the temperature axis is related to the activation energy provided due allowance is made for the possible presence of a measurable induction period. While it does not appear that the DTA method can be developed to the point where these various interrelated factors can be measured individually and quantitatively, a great deal of comparative information can nevertheless be obtained.

The DTA curves illustrate in a very graphic manner what may well be the cause of the occasional disastrous explosions which have occurred with ammonium nitrate stored in bulk. NH_4NO_3 is known to decompose explosively around 300°. The relatively moderate amount of heat liberated by the slow decomposition of pure NH_4NO_3, which may be occurring at ambient temperatures, may be dissipated even from the interior of a large mass without the temperature rising to the explosion point (which may differ from 300° due to the pressure in a large mass). However, if an appreciable concentration of chloride impurity were present, even in localized spots, the highly exothermic nature of the chloride-induced reaction, as illustrated by Figs. 1 and 2, could cause the temperature to rise locally until an explosive condition resulted. This would be aggravated by the fact that the surrounding volume would sinter, plugging the pores, and the pressure would rise due to the gaseous products evolved. The location of the DTA maxima along the horizontal temperature scale in Figs. 1 and 2 is of course dependent on the constants of the present apparatus and under other conditions the chloride-catalyzed reaction could become significant at much lower temperatures. This reaction for example has an appreciable rate already at around 160°. The significant point shown up by the DTA curves is that, once this reaction is set off, it raises the temperature extremely rapidly relative to the decomposition of pure NH_4NO_3. Other impurities than chloride might have the same effect but chloride would appear to be one of the most likely to be present.

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Thallous Complexes in Chloride Solutions[1]

BY KUO-HAO HU AND ALLEN B. SCOTT

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Previous work[2-4] suggests that the luminescence of solutions of alkali halides containing thallium may be due to thallium halide complexes. Some evidence of complex formation was given by

[1] Supported by the Office of Ordnance Research. Published with the approval of the Oregon State College Monographs Committee, Research Paper No. 260, Department of Chemistry, School of Science.

[2] B. E. Gordon and A. Schischlowski, *Phys. chim. Acta U.S.S.R.*, **13**, 247 (1940).

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[4] P. Pringsheim, *J. Chem. Phys.*, **16**, 241 (1948).

Pringsheim and Vogels[5] and Fromherz,[6] who studied the absorption and emission spectra of luminescent chloride solutions. The present investigation is one of a series carried out to determine whether thallous complexes exist in chloride solutions.

The variation of solubility of a difficultly soluble salt with increasing concentration of an added salt having a common ion is useful in determining the formulas and dissociation constants of complexes which may be formed. If the solubility passes through a minimum, there are convenient methods for obtaining the number of anions coördinate to the cation. The solubility of thallous chloride in solutions containing excess chloride has been reported[7,8]; however, these reports deal with chloride ion concentrations up to 0.3 *M* only in aqueous solutions, and up to 2.0 *M* in mixed solvents, and no minimum points in the solubility curves have been found. We have found minimum points at higher chloride concentrations, which have assisted greatly in analyzing the solubility data and which confirm the existence of complex ions.

Experimental

The salts used were C.P., further purified by recrystallization from distilled water. Potassium chloride, sodium chloride and ammonium chloride solutions were prepared by weight. The solutions were agitated with excess thallous chloride in sealed Pyrex flasks, thermostated at 25 ± 0.01°. The temperature was measured by means of a Beckman thermometer calibrated against a platinum resistance thermometer having a National Bureau of Standards calibration.

The attainment of equilibrium was verified by periodically analyzing samples of solution until no further variation of composition with time was observed. Saturation was approached both from under-saturation and over-saturation for potassium chloride solutions, there being no significant difference in the results of the two procedures.

Tl^I was determined by oxidation with standard potassium iodate, using an iodine monochloride solution, prepared according to Jamieson,[9] as an indicator. A microburet, graduated in 0.01 ml., was used for the titration. The color change at the end-point could be detected upon the addition of 0.03 ml. of 0.001 *M* potassium iodate. At least four determinations were made for each concentration of added salt; the results given are averages.

Analysis of the composition of the solid phase in equilibrium with the solution was carried out by filtering and pressing all the solution out of the solid with filter paper, washing the solid with ether and drying to constant weight. It was then dissolved in sufficient water and the solution was analyzed for thallium. The solid in equilibrium with the sodium chloride and ammonium chloride solutions was found to be pure thallous chloride. The solid in equilibrium with the more concentrated potassium chloride solutions was found to contain as much as 7% potassium chloride.

Results

The solubility of thallous chloride in potassium chloride, sodium chloride and ammonium chloride solutions is given in Table I. Curves of solubility, in volume units, against chloride ion concentration, are shown in Fig. 1.

The most outstanding result is the occurrence of minima in the solubility curves, which indicates the formation of complex ions of the type $TlCl_q^{-(q-1)}$, where $q > 1$. It has been shown previously[7,10] that neutral TlCl exists in chloride solutions containing thallium.

TABLE I

SOLUBILITY OF THALLOUS CHLORIDE IN CHLORIDE SOLUTIONS

Concn. of added salt, mole/1000 g. H_2O	Concn. of TlCl, mmole/1000 g. H_2O Added salt KCl	NaCl	NH_4Cl
0.1	3.59	3.70	3.70
0.2	2.51		
0.4		1.86	
0.5	1.91		1.83
0.8		1.56	
1.0	1.76	1.52	1.59
1.5	1.85	1.52	1.62
2.0	1.92	1.64	1.66
2.5	2.08		
3.0	2.36	1.85	1.77
3.5	2.62		
4.0	2.99	2.15	1.99
4.2	3.00	2.21	2.09
4.4	3.08		2.17
4.5	3.10	2.31	2.21

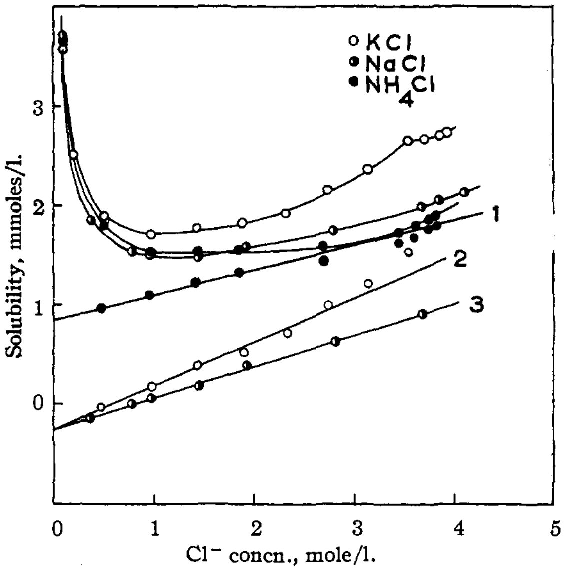

Fig. 1.—Solubility of thallous chloride in solutions of potassium chloride, sodium chloride and ammonium chloride: curves 1–3, $S - (Tl^+)$. Add 1 to ordinates of curves 2 and 3.

We assume initially that thallium is present as Tl^+, TlCl and $TlCl_2^-$. The data may be analyzed on this basis to give the constant solubility of the molecular TlCl. This datum may in turn be used with the solubility at the minimum to give a value of *q*, which should be 2 if the initial assumption is valid.

The concentrations of the species assumed to be present in a saturated solution are related by

$$(Tl^+) = K_s/(Cl^-)f_\pm^2 \quad (1)$$
$$(TlCl) = K_s/K_d \quad (2)$$
$$(TlCl_2^-) = (TlCl)(Cl^-)/K_2 \quad (3)$$
$$S = (Tl^+) + (TlCl) + (TlCl_2^-) \quad (4)$$

where the brackets represent molar concentrations, and

K_s = solubility product of thallous chloride = 0.000192[7]
$f_\pm$ = mean ionic activity coefficient

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K_d = dissociation constant of TlCl; $\mathrm{TlCl} = \mathrm{Tl}^+ + \mathrm{Cl}^-$
K_2 = first dissociation constant of $\mathrm{TlCl_2}^-$; $\mathrm{TlCl_2}^- = \mathrm{TlCl} + \mathrm{Cl}^-$
S = solubility of thallous chloride, mole/liter

Values of $f_\pm$ given by Harned[11] for potassium chloride and sodium chloride solutions, and by Pearce and Pumplin[12] for ammonium chloride solutions, corrected for use with volume concentrations, were used to calculate (Tl^+).

Equation 2 shows that (TlCl) is constant at all concentrations of the added salt subject only to the condition that the activity coefficient of the neutral TlCl and the activity of the water are constant. Combining (3) and (4)

$$S - (\mathrm{Tl}^+) = (\mathrm{TlCl}) + \frac{(\mathrm{TlCl})}{K_2}(\mathrm{Cl}^-)$$

We see that a plot of $S - (\mathrm{Tl}^+)$ against (Cl^-) should give a straight line. The intercept at $(\mathrm{Cl}^-) = 0$ is (TlCl); the slope is $(\mathrm{TlCl})/K_2$. K_d is given by equation 2.

From curves 1–3, Fig. 1, we see that such plots for the three solutions studied are nearly linear, at least in the concentration range where we expect (TlCl) to be really constant.

Similar analyses were made assuming that the value of q for the complex was greater than two. In these cases some uncertainty is introduced in choosing an appropriate activity coefficient for the multiply-charged complex ion; following the Debye–Hückel theory, f for such ions was taken as $Z^2 f_\pm$, where Z is the ionic charge and $f_\pm$, as before, is the mean value for the 1–1 electrolyte. If, for example, $\mathrm{TlCl_4}^{---}$ is assumed to be present in addition to Tl^+ and TlCl, a plot of $S - (\mathrm{Tl}^+)$ against $9f_\pm(\mathrm{Cl}^-)^3$ should be linear; in reality such a plot shows very pronounced curvature over the entire concentration range, far exceeding any curvature which might have been introduced by an error in the assumed activity coefficient, and we must conclude $\mathrm{TlCl_4}^{---}$ is definitely not the only negatively charged complex ion present. This was found true for other species of $q > 2$.

We consider now the possibility that ions of $q > 2$ are present in addition to $\mathrm{TlCl_2}^-$. Then

$$S - (\mathrm{Tl}^+) = (\mathrm{TlCl}) + \frac{(\mathrm{TlCl})}{K_2}(\mathrm{Cl}^-) + A(\mathrm{Cl}^-)^2 + B(\mathrm{Cl}^-)^3 + \ldots,$$

where $A, B \ldots$ are positive and involve (TlCl), dissociation constants, and activity coefficients. If $A, B, \ldots$ are not zero, there should be upward curvature in curves 1 to 3 of Fig. 1. This curvature is noted for KCl solutions at concentrations greater than about 2.5 *M;* however, it may be estimated from the curve that at 3 *M* the $\mathrm{TlCl_2}^-$ concentration is at least 10 times that of complex ions of $q > 2$.

It is concluded that $\mathrm{TlCl_2}^-$ is the only complex ion present in appreciable concentration, except in the KCl solutions of high concentration.

Further confirmation is provided by the use of an equation given by Reynolds and Argersinger,[13] modified to allow its use in solutions of high ionic strength

$$q = \frac{S_m C_m f_\pm^2}{S_m C_m f_\pm - K_s}$$

where S_m is the ionic concentration of thallous chloride at the point of minimum solubility, to include simple and complex ions but not neutral molecules such as TlCl, C_m is the chloride ion concentration at the minimum, and $f_\pm$ is the mean ionic activity coefficient for the thallium-containing ions. The equation is valid for the case in which only one complex ion exists in appreciable concentration, which is the case we have assumed initially. On the basis of the initial assumption, both the simple and complex ions of thallium are singly charged and thus $f_\pm$ for the added chloride is appropriate. The values of q calculated from the minimum points of the solubility curves are given in Table II; in all cases q was nearly 2, a value consistent with our assumption that $\mathrm{TlCl_2}^-$ is the only negatively charged complex ion present in appreciable concentration in the range investigated.

TABLE II

DISSOCIATION CONSTANTS OF THALLOUS COMPLEXES AT 25°

Added salt	C_m, mole/l.	S_m, mole/l.	q	K_D	K_2
KCl	0.97	0.00096	2.2	0.26	1.7
NaCl	1.3	.00073	1.8	.26	2.3
$\mathrm{NH_4Cl}$	1.3	.00075	1.9	.23	3.0
Av. for NaCl and $\mathrm{NH_4Cl}$ solutions				.25	2.7

The dissociation constants of TlCl and $\mathrm{TlCl_2}^-$ are also given in Table II. Since the solid phase was not pure over the entire range of potassium chloride solutions, the dissociation constants so obtained were not included in the average. Onsager[10] reported 0.31, and Davies[14] 0.30, for K_D at 18°, in good agreement with our value, allowing for the temperature difference.

The pronounced discontinuity in the slope of the solubility curve in potassium chloride solutions at 3.5 *M* merits further investigation. We suppose it to be due to a change in composition of the solid phase with varying potassium concentration of the solution.

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Some Sulfur Compounds as Polymerization Sensitizers

BY R. J. KERN

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It has long been suspected that rubber chemicals operate *via* free radical mechanisms in vulcanization processes. A convenient tool for studying radical generation involves vinyl polymerization. This work reports the use of several sulfur containing rubber chemicals as polymerization sensitizers. Some sulfur-radical generating compounds have been so used before, diazothioethers as thermal[1] and disulfides as photo[2] sensitizers.

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