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## Spectrophotometric Study of Equilibria in Hydrochloric Acid Solutions of Tellurium(IV)

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Tellurium(IV) in strongly acidic solutions forms chloro-complexes of the composition  $\text{HTeCl}_5 \cdot 5\text{H}_2\text{O}$  (an unstable yellow compound)<sup>1</sup>, salts with composition  $\text{MTeCl}_5$  (where  $\text{M}^+ = \text{Rb}^+$ ,  $\text{K}^+$ , or  $\text{Cs}^+$ )<sup>2</sup>, and also salts with organic bases<sup>3</sup>. All these compounds are yellow and have low stability. Compounds containing the  $[\text{TeCl}_5]^{2-}$  ion are more stable. The salts  $\text{A}_2\text{TeCl}_6$  (where  $\text{A}^+ = \text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ , or the cation of an organic base) separate as yellow crystals from concentrated hydrochloric acid solutions when the corresponding chloride  $\text{ACl}$  is added<sup>4</sup>. Iofa and coworkers compared the absorption spectra of organic extracts containing  $\text{Te}^{\text{IV}}$  chloro-complexes and aqueous hydrochloric acid solutions of  $\text{Te}^{\text{IV}}$ , and showed that the latter contain a number of complexes, chiefly  $[\text{TeCl}_5]^{2-}$  ( $\lambda_{\text{max}} = 372 \pm 4 \text{ nm}$ ) and  $[\text{TeCl}_5(\text{H}_2\text{O})]^-$  ( $\lambda_{\text{max}} = 268 \pm 2 \text{ nm}$ )<sup>5</sup>. By analogy with the complexes of antimony and tin, these authors assumed the existence of three tetrachloro-complexes with compositions  $[\text{TeCl}_4(\text{H}_2\text{O})_2]$ ,  $[\text{Te}(\text{OH})\text{Cl}_4(\text{H}_2\text{O})]^-$ , and  $[\text{Te}(\text{OH})_2\text{Cl}_4]^{2-}$ . Mizumachi<sup>6</sup> studied ion exchange from mixed  $\text{LiCl-HCl}$  solutions, and concluded that anionic chloro-complexes of tellurium are present in solutions with a total ionic strength of 10 M. At lower ionic strength (2.0-4.0 M) the solutions contain hydroxo-complexes.

The present paper puts forward some ideas regarding the composition of the complexes absorbing in the range 340-440 nm, and gives the formation constants for these complexes, the formation constant of  $[\text{TeOCl}_4]^{2-}$ , and the equilibrium constant characterising the conversion of  $[\text{TeOCl}_4]^{2-}$  into  $[\text{TeCl}_4(\text{H}_2\text{O})_2]$ .

### EXPERIMENTAL

The absorption spectra were recorded on an SF-4 spectrophotometer. The solutions for the photometric studies contained  $2.5 \times 10^{-4} \text{ M}$ ,  $5.0 \times 10^{-4} \text{ M}$ , and  $1.0 \times 10^{-3} \text{ M Te}^{\text{IV}}$  and different concentrations of hydrochloric acid ( $5.0 \times 10.0 \text{ M}$ ). The starting material for the preparation of the solutions was metallic tellurium with purity 99.99%. The spectra of some of the solutions are given in Figs. 1 and 6. The dependence of the optical density on the HCl concentration, and the mean molar absorptivities  $\epsilon$  are given in Table 1.

Analysis of the absorption spectra (Fig. 1) shows that at a constant tellurium concentration the optical density increases with increase in the HCl concentration, but does not reach a constant value in any range of HCl concentrations; this is possible if the chloro-complexes of tellurium have a low stability. Apparently at any HCl concentration the solution contains not less than two tellurium compounds. If the light absorption is due to the highest complex or, for two absorbing species, if the higher complex has a larger molar absorptivity, the latter can be found by Yatsimirskii's method, according to which  $\epsilon$  for

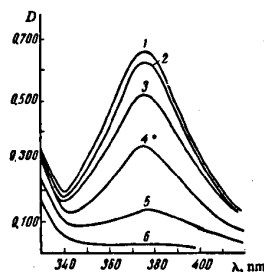


Figure 1. Absorption spectra of solutions of tellurium(IV) in hydrochloric acid with varying concentration.  
 $c_{\text{Te}} = 2.5 \times 10^{-4} \text{ M}$ ;  $c_{\text{HCl}} (\text{M})$ :  
 1) 10.0, 2) 9.0, 3) 8.0, 4) 7.0, 5) 6.0, 6) 5.0.

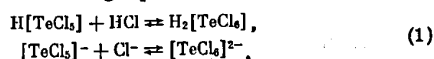
Table 1. Optical density and mean molar absorptivity of solutions of tellurium(IV) in hydrochloric acid.

HCl concn., M	$c_{\text{Te}} \cdot 10^4$	$c_{\text{H}_2\text{O}}$	355 nm		360 nm		365 nm		370 nm		375 nm		380 nm		385 nm		390 nm		395 nm		400 nm		410 nm	
			D	$\epsilon$	D	$\epsilon$	D	$\epsilon$	D	$\epsilon$	D	$\epsilon$	D	$\epsilon$	D	$\epsilon$	D	$\epsilon$	D	$\epsilon$	D	$\epsilon$	D	$\epsilon$
10.0	201	0.292	0.373	1492	0.471	1884	0.555	2220	0.526	2504	0.660	2640	0.645	2580	0.579	2316	0.485	1932	0.393	1572	0.318	1272	0.197	788
9.5	161	0.332	0.358	1432	0.453	1812	0.537	2148	0.507	2428	0.640	2560	0.630	2520	0.568	2272	0.476	1904	0.380	1520	0.308	1232	0.192	768
9.0	123	0.368	0.340	1360	0.429	1716	0.512	2048	0.483	2332	0.618	2472	0.613	2452	0.550	2200	0.464	1856	0.373	1492	0.301	1204	0.186	744
8.5	95.7	0.406	0.325	1300	0.409	1636	0.490	1960	0.463	2212	0.586	2344	0.587	2348	0.523	2092	0.441	1764	0.360	1440	0.288	1152	0.181	724
8.0	74.8	0.454	0.287	1148	0.354	1416	0.426	1704	0.483	1932	0.519	2076	0.513	2052	0.455	1820	0.390	1560	0.316	1264	0.256	1024	0.159	636
7.5	55.8	0.500	0.235	940	0.290	1160	0.349	1396	0.395	1580	0.430	1720	0.429	1716	0.380	1520	0.321	1284	0.266	1064	0.216	864	0.134	536
7.0	42.4	0.553	0.185	740	0.220	880	0.260	1040	0.296	1184	0.320	1280	0.320	1280	0.282	1128	0.243	972	0.201	804	0.162	648	0.097	388
6.5*	32.5	0.609	—	—	—	—	—	—	0.375	750	0.425	850	0.423	846	0.373	746	0.332	664	0.280	560	0.195	390	0.112	224
6.0	25.0	0.658	0.090	360	0.100	400	0.110	440	0.124	496	0.137	543	0.138	552	0.122	488	0.103	412	0.086	344	0.071	284	—	—
5.5**	18.7	0.695	—	—	—	—	—	—	0.202	202	0.212	212	0.213	213	0.192	192	0.162	162	0.134	134	0.107	107	—	—

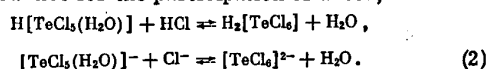
\* Optical density measured for a solution with concentration  $5 \times 10^{-4} \text{ M}$ .\*\* Optical density measured for a solution with concentration  $1 \times 10^{-3} \text{ M}$ .

the higher complex is determined graphically by extrapolating the value of the mean molar absorptivity  $\bar{\epsilon} = f(1/a_{\text{Cl}^-})$  for  $a_{\text{Cl}^-} \rightarrow \infty$  at constant tellurium concentration ( $\bar{\epsilon} = D/c_{\text{total}}$ , where  $c_{\text{total}}$  is the total concentration of tellurium in the solution).

Since hydrochloric acid solutions of  $\text{Te}^{\text{IV}}$  contain various complexes, it is necessary, in the determination of the molar absorptivity of the complex  $[\text{TeCl}_6]^{2-}$  ( $\epsilon_6$ ), to examine the equilibria in the most concentrated HCl solutions. In this instance it is possible to take into account only the two highest complexes, for which the equilibrium can be represented by the following equations



or, with allowance for the participation of water,



The equilibrium constant (formation constant) in the last instance has the form

$$K_6 = \frac{[\text{TeCl}_6^{2-}] \cdot [\text{H}_2\text{O}]}{[\text{TeCl}_5(\text{H}_2\text{O})^-] \cdot [\text{Cl}^-]}, \quad (3)$$

where the activity of each ion can be expressed in terms of its concentration and activity coefficient:

$$[\text{TeCl}_6^{2-}] = f_6 c_6,$$

$$[\text{TeCl}_5(\text{H}_2\text{O})^-] = f_5 c_5, \quad [\text{Cl}^-] = a_{\text{Cl}^-} = f_{\text{Cl}} c_{\text{Cl}}.$$

The concentration of tellurium-containing species is small, and at a high ionic strength created by hydrochloric acid the activity coefficients of these species are probably close to one another. In this instance the ratio of the activities of the tellurium-containing complexes can be replaced by the ratio of their analytical concentrations. The activity of the chloride ion (and subsequently the hydrogen ion activity, which is equal to the chloride ion activity) was calculated from the molarity of the HCl and its mean activity coefficients, taken from the data of Robinson and Stokes<sup>7</sup>. The activity of water was calculated from the vapour pressure of water above hydrochloric acid solutions<sup>8</sup>.

With allowance for the foregoing, Eqn. (3) can be written in the form

$$K_6 = \frac{c_6 \cdot a_{\text{H}_2\text{O}}}{c_5 \cdot a_{\text{Cl}^-}}. \quad (4)$$

The optical density for one absorbing species is given by the equation

$$D = \epsilon_0 \cdot c_0. \quad (5)$$

The total concentration of tellurium in highly concentrated solutions can be taken as the sum of the concentrations of the two complexes

$$c_{\text{total}} = c_0 + c_5. \quad (6)$$

Combination of Eqns. (4), (5), and (6) gives

$$\bar{\epsilon} = \epsilon_0 - \frac{\epsilon_0 \cdot a_{\text{H}_2\text{O}}}{K_6 \cdot a_{\text{Cl}^-}}. \quad (7)$$

The graphical solution of Eqn. (7) is given in Fig. 2. In general, it is found that  $\bar{\epsilon}$  is approximately linearly dependent on  $\bar{\epsilon} \cdot (a_{\text{H}_2\text{O}}/a_{\text{Cl}^-})$  for 8.5–10.0 M HCl solutions. The values of the slopes differ significantly, however, for the short-wave and long-wave sides of the absorption band. The slope has a smaller absolute magnitude in the second instance. This can be regarded as a consequence of the

presence of the second absorbing species, the absorption band of which is displaced towards longer wavelengths. The monotonic increase in  $\bar{\epsilon}$  with increase in chloride ion concentration indicates that the value of  $\epsilon_0$  is greater than that of  $\epsilon_5$ , so that Yatsimirskii's method can be used. The molar absorptivities of  $[\text{TeCl}_6]^{2-}$  at various wavelengths were determined by graphical extrapolation from Fig. 2.

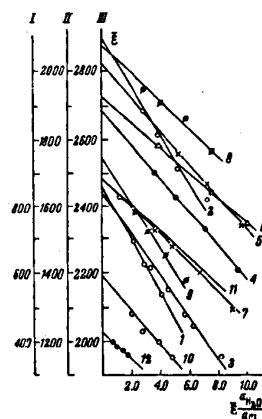


Figure 2. Graphical determination of  $\epsilon_0$  and  $K_6$  from Eqn. (10). The data relate to absorption at the following wavelengths (nm): (scale I): 1) 410; 2) 420; (scale II): 1) 355; 2) 360; 3) 390; 4) 395; 5) 400; (scale III): 1) 365; 2) 370; 3) 375; 4) 380; 5) 385.

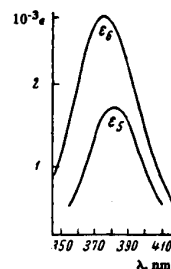


Figure 3. Absorption bands for the individual complexes  $\text{TeCl}_6^{2-}$  and  $[\text{TeCl}_5(\text{H}_2\text{O})]^-$ .

To determine more precisely the shape of the absorption band of the higher complex, to which an octahedral structure is assigned<sup>9</sup>, we used the equation for the probability curve

$$\sqrt{\lg \frac{\epsilon_0}{\epsilon}} = \frac{2\sqrt{\lg 2}}{\Delta\nu} (|\nu_0 - \nu|),$$

where  $\epsilon_0$  is the molar absorptivity at the maximum point,  $\nu_0$  the wave number at the absorption maximum, and  $\epsilon$  the molar absorptivity at an arbitrary value of  $\nu$ .

The shape of the  $\epsilon_0$  band is shown in Fig. 3. The absorption maximum of the  $[\text{TeCl}_6]^{2-}$  ion lies at  $\lambda = 375 \pm 2$  nm.

In the determination of the formation constant  $K_6$ , allowance was made for the absorption of two species  $[\text{TeCl}_6]^{2-}$  and  $[\text{TeCl}_5(\text{H}_2\text{O})]^-$  and the optical density of the solution is given by the equation

$$D = \epsilon_6 c_6 + \epsilon_5 c_5, \quad (8)$$

where  $\epsilon_5$  is the molar absorptivity of  $[\text{TeCl}_5(\text{H}_2\text{O})]^-$ . Using (4), (6), and (8), we obtain

$$\bar{\epsilon} = \epsilon_5 + \frac{K_6(\epsilon_6 - \epsilon_5)a_{\text{Cl}^-}}{a_{\text{H}_2\text{O}}}. \quad (9)$$

$K_6$  and  $\epsilon_5$  were found graphically from the dependence of  $\bar{\epsilon}$  on  $(\epsilon_6 - \epsilon_5)a_{\text{Cl}^-}/a_{\text{H}_2\text{O}}$  from the values of  $\bar{\epsilon}$  for 8.5–10.0 M HCl solutions and the more accurately determined values of  $\epsilon_6$  (Fig. 4). The equation for the probability curve was again used to determine more precisely the values of  $\epsilon_5$ . The values obtained for  $K_6$ ,  $\epsilon_6$ ,  $\epsilon_5$ , and  $\epsilon_{5\text{corrected}}$  are given in Table 2, and the shape of the absorption band of the complex  $[\text{TeCl}_5(\text{H}_2\text{O})]^-$  is given in Fig. 3.

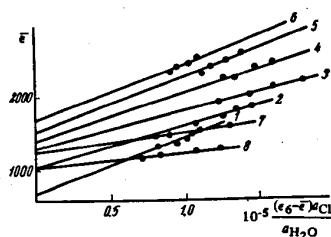


Figure 4. Graphical determination of  $\epsilon_5$  and  $K_6$  from Eqn. (12) for  $c_{\text{HCl}} = 8.5\text{--}10.0$  M. The data relate to the apparent molar absorptivities at the following wavelengths: 1) 355; 2) 360; 3) 365; 4) 370; 5) 375; 6) 380; 7) 395; 8) 400.

Table 2. Molar absorptivities of the complexes  $[\text{TeCl}_6]^{2-}$  ( $\epsilon_6$ ) and  $[\text{TeCl}_5(\text{H}_2\text{O})]^-$  ( $\epsilon_5$ ) and formation constants.

$\lambda$	$\epsilon_6$	$\epsilon_5$	$\epsilon_5^{\text{corrected}}$	$10^3 K_6$
355	1644	680	520	7.5
360	2095	1030	740	5.6
365	2480	1300	1070	5.3
370	2733	1400	1380	7.0
375	2820	1500	1600	6.3
380	2735	1690	1690	7.0
385	2510	1590	1660	6.2
390	2200	1525	1500	4.0
395	1760	1220	1250	3.0
400	1451	1020	980	—
mean $(6.4 \pm 0.7) \cdot 10^{-2}$				

With decrease in the HCl concentration below 8.5 M, the decrease in the optical density is greater than that which should be observed in the presence of the two highest complexes alone. The sharp fall in optical density can be attributed to the appearance in solution of tetrachloro-complexes of tellurium, which do not absorb in the range being considered. The compositions of the tetrachloro-complexes can be represented by the three formulae  $[\text{TeCl}_4(\text{H}_2\text{O})_2]$ ,  $[\text{Te}(\text{OH})\text{Cl}_4(\text{H}_2\text{O})]^-$ , and  $[\text{Te}(\text{OH})_2\text{Cl}_4]^{2-}$ .

These complexes are, as it were, products of successive stages in the acidic dissociation of the first complex. Since the acidic dissociation should depend on the  $\text{H}^+$  ion activity in the solution, it can be neglected in the more concentrated HCl solutions (7.5–8.5 M). In these solutions the equilibrium between the tetrachloro-complex and the pentachloro-complex is given by the equation



with equilibrium constant

$$K_5 = \frac{c_5 \cdot a_{\text{H}_2\text{O}}}{c_4 \cdot a_{\text{Cl}^-}}. \quad (11)$$

From (4), (8), (11), and the tellurium balance

$$c_{\text{total}} = c_6 + c_5 + c_4 \quad (12)$$

we obtain

$$\frac{K_5(\epsilon_6 - \epsilon_5)}{a_{\text{H}_2\text{O}}/a_{\text{Cl}^-}} + (\epsilon_5 - \bar{\epsilon}) = \bar{\epsilon} \frac{a_{\text{H}_2\text{O}}}{a_{\text{Cl}^-} \cdot K_5}. \quad (13)$$

From this equation we can determine  $K_5$  analytically, using the values of  $\bar{\epsilon}$  for solutions 7.5–8.0 M with respect to HCl (Table 3). Further decrease in the hydrochloric acid concentration is probably associated with the following equilibria

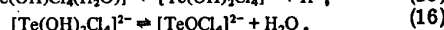
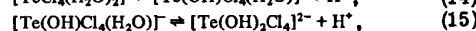
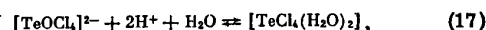


Table 3. Values of  $K_5$  obtained from Eqn. (13).

$c_{\text{HCl}}, \text{M}$	$10^2 K_5$ for $\lambda, \text{nm}$			
	385	390	395	400
8.0	1.94	1.55	1.51	1.53
7.5	1.61	1.33	1.40	1.45
Mean $K_5 = (1.48 \pm 0.08) \cdot 10^{-2}$				

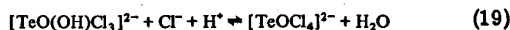
Hydroxo-compounds of  $\text{Te}^{\text{IV}}$  are extremely unstable, and readily give up water and are converted into oxo-compounds. For example, tellurium(IV) oxide chloride and oxide nitrate are familiar compounds, and tellurous acid readily loses water and is converted into the dioxide on gentle heating. It may thus be assumed that the relative concentration of  $[\text{Te}(\text{OH})\text{Cl}_4(\text{H}_2\text{O})]^-$  and  $[\text{Te}(\text{OH})_2\text{Cl}_4]^{2-}$  ions is comparatively low and can be neglected in the equations for the tellurium balance. Thus Eqns. (14), (15), and (16) can be represented by the overall equation



which is characterised by the equilibrium constant

$$K_4' = \frac{c_4}{c_4' \cdot a_{\text{H}_2\text{O}} \cdot a_{\text{H}^+}^2}, \quad (18)$$

where  $c_4'$  relates to the concentration of  $[\text{TeOCl}_4]^{2-}$ . In addition to these equilibria, with decrease in the HCl concentration it is also possible to make allowance for the appearance of trichloro-complexes in the solution, taking part in the equilibrium



which is characterised by the formation constant

$$K_4 = \frac{c_4' \cdot a_{H_2O}}{c_3 \cdot a_{Cl^-} \cdot a_{H^+}} \quad (20)$$

Eqns. (4), (8), (11), (18), and (20), and the equation for the tellurium balance

$$c_{\text{total}} = c_0 + c_3 + c_4 + c_4' + c_5 \quad (21)$$

after slight transformation, give the equation

$$\frac{a_{Cl^-}}{a_{Cl^-}} \cdot \left[ \frac{K_0 K_5 (e_0 - e) a_{Cl^-}^2}{e} + \frac{K_5 (e_0 - e) a_{Cl^-}}{e} \right] - a_{H_2O} = \frac{1}{K_4'} + \frac{1}{K_4 K_4'} \cdot \frac{a_{H_2O}}{a_{Cl^-}^2} \quad (22)$$

(assuming  $a_{Cl^-} = a_{H^+}$ ).

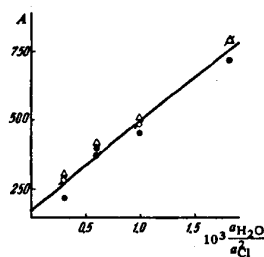


Figure 5. Graphical determination of  $K_4$  and  $K_4'$  from Eqn. (22). The quantity plotted on the axis of ordinates is

$$A = \frac{a_{Cl^-}}{a_{Cl^-}} \cdot \left[ \frac{K_0 K_5 (e_0 - e) a_{Cl^-}^2}{e} + \frac{K_5 (e_0 - e) a_{Cl^-}}{e} \right] - a_{H_2O}$$

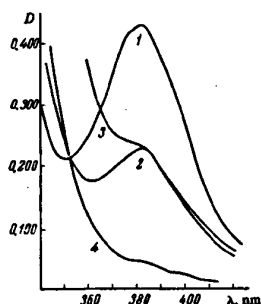


Figure 6. Absorption spectra of solutions of tellurium(IV) in moderately concentrated hydrochloric acid: 1)  $c_{Te} = 5 \times 10^{-4}$  M,  $c_{HCl} = 7.0$  M; 2)  $c_{Te} = 5 \times 10^{-4}$  M,  $c_{HCl} = 6.5$  M; 3)  $c_{Te} = 1 \times 10^{-3}$  M,  $c_{HCl} = 5$  M; 4)  $c_{Te} = 1 \times 10^{-3}$  M,  $c_{HCl} = 4.0$  M.

The graphical solution of Eqn. (22) in which data on the optical density are used for 5.5–7.0 M HCl solutions is shown in Fig. 5. Results for wavelengths of 385, 390, 395, and 400 nm were used, since the short-wave side of the

overall absorption band shows a shoulder which is particularly clearly defined as the tellurium concentration is increased (Fig. 6). 2.0–5.0 M HCl solutions apparently contain a third species absorbing in the range 300–380 nm. The mean value of the constants characterising equilibria (17) and (19) are

$$K_4' = (6.3 \pm 1.3) \cdot 10^{-3} \text{ and } K_4 = (4.8 \pm 0.8) \cdot 10^{-4}.$$

Further decrease in the HCl concentration displaces the equilibrium towards the formation of  $[TeO(OH)_2Cl_2]^{2-}$ ,  $[TeO(OH)_2Cl]^-$ , and  $[TeO(OH)_2]$ . Further calculations which involve the 340–440 nm band are difficult, however, since it is necessary to use a large number of interrelated quantities.

## SUMMARY

1. The absorption spectra of solutions of tellurium(IV) in hydrochloric acid with different concentration have been recorded in the range 340–440 nm.
2. The absorption bands corresponding to the individual complexes  $[TeCl_5]^{2-}$  ( $\lambda_{\text{max}} = 375 \pm 2$  nm) and  $[TeCl_5(H_2O)]^-$  ( $\lambda_{\text{max}} = 381 \pm 2$  nm) have been isolated.
3. The consecutive formation constants have been calculated for the complexes  $[TeCl_5]^{2-}$  ( $K_5 = (6.4 \pm 0.7) \times 10^{-3}$ ),  $[TeCl_5(H_2O)]^-$  ( $K_6 = (1.48 \pm 0.08) \times 10^{-3}$ ), and  $[TeOCl_4]^{2-}$  ( $K_4 = (4.8 \pm 0.8) \times 10^{-4}$ ).
4. The equilibrium constant for the conversion of oxo-tetrachlorotellurate(IV) into tetrachlorodiotellurium(IV) has been calculated; the value found is  $(6.3 \pm 1.3) \times 10^{-3}$ .

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## Complex Oxide Fluorides of Zirconium and Hafnium with Potassium

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We have established previously that precipitation of zirconium and hafnium hydroxides from solutions of  $K_2ZrF_6$  and  $K_2HfF_6$  with ammonia and alkalis involves the formation