TABLE I

COMPARISON OF YIELDS OF $KNO_2$ AND $Pb(NO_3)_2$

| | Dose, e.v./g. × 18 × $10^{-19}$ | $O_2$, μmoles/g. | $NO_2$, μmoles/g. | $G/O_2$ | $G/NO_2^-$ |
|---|---|---|---|---|---|
| $KNO_3$ | 160 | 18.8 | 36.4 | 0.71 | 1.38 |
| | 65.5 | 7.5 | 13.5 | .70 | 1.25 |
| | 55.5 | 6.5 | 12.5 | .71 | 1.36 |
| $PbNO_3$ | 90.2 | 6.3 | 6.2 | .42 | 0.42 |
| | 59.1 | 4.07 | 4.08 | .42 | 0.42 |
| | 261.0 | 9.78 | 18.65 | .23 | 0.43 |
| | 161 | 7.96 | ... | .31 | .. |

not removed by boiling. The absorption spectra of this solution (curve A,[6] Fig. 2) when compared to that of the non-irradiated salt, shows that $NO_2^-$ is the only new chemical species. The only plausible explanation for the amber color is that it is due to a colloidal suspension and the only feasible substance to be in colloidal suspension is PbO.

A possible mechanism for the decomposition of $Pb(NO_3)_2$ and perhaps other inorganic salts containing both covalent and ionic bonds is that the electronic excitation energy received is rapidly transferred to lattice vibrational energy. This vibrational energy may be assumed to cause high local temperatures[7a,b] which are sufficient to thermally decompose the salt. The products then should be similar to those found in the thermal decomposition. A thermal mechanism is consistent with the observation of Cunningham and Heal[2a] that the yield (*G*-values) of the nitrates is proportional to the "Free Volume" as suggested by Hennig, Lees and Matheson.[5]

There is, of course, no positive evidence to support a thermal mechanism or a free radical mechanism.[2b] However, reflectance spectra of irradiated $Pb(NO_3)_2$ and $KNO_3$ (Fig. 3) show an absorption maximum at about 3500 Å. A similar peak at about 3600 Å. is found in the reflectance spectra of γ-ray irradiated sodium azide.[8] Heat treatment of unirradiated $NaN_3$ crystals also produces an absorption band at about 3600 Å. indicating that this band is connected with the decomposition of $NaN_3$ brought about either by irradiation or thermal treatment.

It is believed that the band at 3400 Å. found in irradiated $Pb(NO_3)_2$ is associated with the decomposition of the material; *i.e.*, it is possible that the band could be associated with metastable nitrate ions. Heating irradiated $Pb(NO_3)_2$ at 60° for several days results in a decrease in the intensity of the band at 3400 Å. with a corresponding decrease in the $NO_2^-$ concentration, but no decrease in the oxygen concentration.

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(6) This curve was extended to 1100 mμ not shown in Fig. 2.

(7) (a) F. Dessauer, *Z. Physik*, **38**, 12 (1923); (b) F. Seitz and J. S. Kohler, "Solid State Physics," Vol. II, Academic Press, New York, N. Y., pp. 351–448.

(8) H. Rosenwasser, R. W. Dreyfus and P. W. Levy, *J. Chem. Phys.*, **24**, 184 (1956).

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[CONTRIBUTION FROM THE SPRAGUE ELECTRIC COMPANY]

# The Dissociation of Tetrachloroiodide Salts

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The total dissociation vapor pressures of the tetrachloroiodide salts $KICl_4$, $RbICl_4$, $NH_4ICl_4$ and $N(CH_3)_4ICl_4$ have been measured over the temperature range 35–90°. Equilibrium pressures are obtained readily with increasing temperature but extremely slowly with decreasing temperature. Evidence is presented that the dissociation of $KICl_4$ proceeds through the dichloroiodide, $KICl_2$, as a solid intermediate rather than directly to KCl as previously reported.

Although the dissociation vapor pressures of polyhalide salts have been studied by many investigators,[1,2,3,4] the evidence does not indicate clearly whether the dissociation reactions proceed directly to the simple halide or through an intermediate, simpler polyhalide in cases where such an intermediate compound exists. The literature is particularly confusing concerning the mode of decomposition of the salts of the $ICl_4^-$ anion.

Caglioti and Centola[4] have measured the equilibrium halogen pressure over potassium tetrachloroiodide using the technique of Ephraim. They concluded that $KICl_4$ dissociates directly to KCl and $ICl_3$, the latter undergoing further dissociation to ICl and $Cl_2$. This would indicate that the dissociation vapor is made up of equal partial pressures of $Cl_2$ and ICl since the $ICl_3$ should be completely dissociated under the experimental conditions used. This conclusion is not thermodynamically compatible, however, with the equilibrium pressure of ICl over $KICl_2$ as measured by Cornog and Bauer.[3] We also have measured the dissociation vapor pressure of $KICl_4$ and have made similar measurements on $RbICl_4$, $CsICl_4$, $NH_4ICl_4$ and $N(CH_3)_4ICl_4$. Our results differ somewhat from those of Caglioti and Centola, and in contrast to their conclusions we have direct evidence that $KICl_2$ is formed as a solid intermediate in the dissociation of $KICl_4$.

## Results

The experimentally obtained dissociation vapor data for the several salts are shown in Fig. 1 as plots of log $p_{mm}$ *versus* the reciprocal absolute temperature. The appropriate constants for expressing the pressures in terms of an equation of the type

$$\log p_{mm} = \frac{A}{T°K.} + B \qquad (1)$$

are given in Table I.

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(1) F. Ephraim, *Ber.*, **50**, 1069 (1917).

(2) H. W. Cremer and D. R. Duncan, *J. Chem. Soc.*, 2243 (1931).

(3) J. Cornog and E. E. Bauer, THIS JOURNAL, **64**, 2620 (1942).

(4) V. Caglioti and G. Centola, *Gazz. chim. ital.*, **63**, 907 (1933).

TABLE I

CONSTANTS FOR EXPRESSING DISSOCIATION PRESSURES IN THE FORM $\log p_{\text{mm}} = \frac{A}{T\ \text{°K.}} + B$

| Salt | A, °K. | B |
|---|---|---|
| $KICl_4$ | 3566.0 | 11.834 |
| $RbICl_4$ | 3230.6 | 10.359 |
| $NH_4ICl_4$ | 3124.6 | 10.631 |
| $N(CH_3)_4ICl_4$ | 2507.3 | 7.861 |

Evidence for the formation of $KICl_2$ as an intermediate in the dissociation of $KICl_4$ was obtained by measuring the e.m.f. of the Ag–$KICl_4$ couple as a function of the decomposition of $KICl_4$. Solid electrolyte, electrochemical cells were prepared in which the anode is silver, the electrolyte a thin film of silver chloride and the cathode a mixture of a polyhalide salt and carbon black in an inert grease substrate. The polyhalide salt serves as a low pressure source of halogen vapor which is the active cathode constituent. Silver chloride is predominantly an ionic conductor and in the form of a thin film (~10 μ) serves as a stable, high impedance electrolyte. The e.m.f. of a Ag/AgCl/polyhalide cell is thus a function of the identity of the most active halogen (or polyhalogen) dissociation vapor present and its equilibrium pressure. Cells made with $KICl_4$ in the cathode have an e.m.f. of 1.04 volts at 25°. When these cells were subjected to elevated temperatures (100–125°) such that the $KICl_4$ was gradually decomposed it was found that in 21 out of 23 cells, the e.m.f. eventually dropped abruptly to 0.89 volt and remained constant at this value for a time comparable with the duration of the original e.m.f. When cells were constructed with cathodes containing $KICl_2$ rather than $KICl_4$ the e.m.f. was found to be 0.89 volt. This is a positive indication of the formation of $KICl_2$ as an intermediate, solid dissociation product by the loss of $Cl_2$ from $KICl_4$.

The dissociation pressures measured for $CsICl_4$ were not significantly different from those found for $RbICl_4$. This led to a suspicion that the $CsICl_4$ might contain $RbICl_4$ and that this impurity was the determining factor for the dissociation vapor pressure. Samples of $CsICl_4$ and $RbICl_4$ were thermally decomposed to the chlorides and analyzed by emission spectroscopy. The following impurity contents were estimated: in the CsCl: ≈0.5% K, ~3% Rb, ~0.01% Na; in the RbCl: >>1% K, ~0.01% Na, >10% Cs. It is assumed that the amount of $RbICl_4$ in the $CsICl_4$ was sufficient to determine the dissociation pressure and the results obtained for $CsICl_4$ have not been included for this reason. A substantial amount of potassium was found in the RbCl; if this was originally present as $KICl_4$ it must have been decomposed to KCl in the vacuum drying operation since the $RbICl_4$ was found to have dissociation pressures distinctly different from those of $KICl_4$ and $KICl_2$. The presence of $CsICl_4$ in the $RbICl_4$ would not be detrimental since the latter should have the higher dissociation pressure.

## Discussion

Our data for the dissociation pressures of $KICl_4$ and those of Caglioti and Centola are compared in Fig. 2. It is seen that the earlier data differ in detail from ours and do not give a straight line on a log *p* *vs.* 1/*T* plot. There was a possibility that this deviation from usual behavior could be justified in two possible ways.

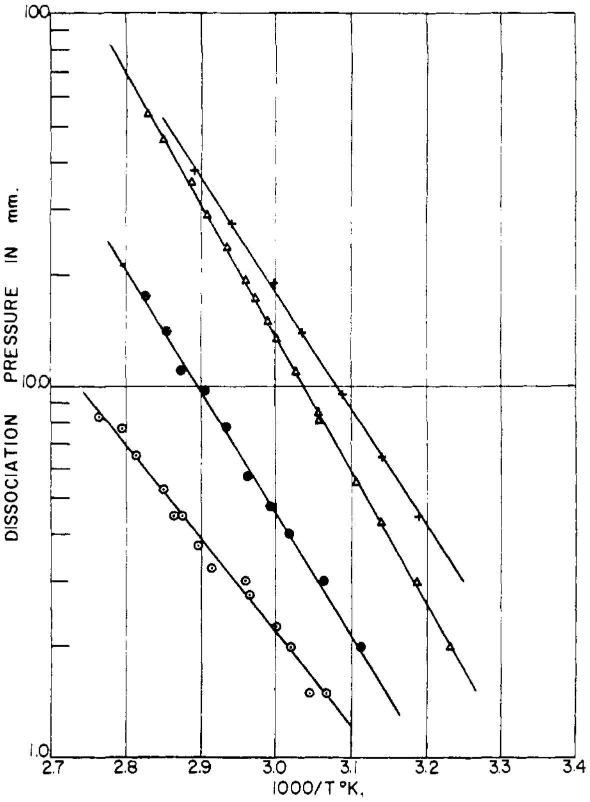

Fig. 1.—Dissociation vapor pressures of tetrachloroiodide salts: +, $NH_4ICl_4$; △, $KICl_4$; ●, $RbICl_4$; ○, $N(CH_3)_4ICl_4$.

For pressures greater than 1 mm. the data could be considered as being made up of two intersecting straight lines representing the equilibrium

$$KICl_4 = KICl_2 + Cl_2 \qquad (2)$$

in the low temperature range with the further dissociation step

$$KICl_2 = KCl + ICl \qquad (3)$$

becoming significant at higher temperatures. If this were the case, one should obtain the high temperature dissociation pressures found by Caglioti and Centola by adding the dissociation pressure of $KICl_2$ to an extrapolation of the low temperature slope into the high temperature region. When this is done using the data of Cornog and Bauer[3] for the dissociation pressure of $KICl_2$, however, no such correlation is obtained.

The other possible explanation involves the assumption that the term containing the heat capacity, $\Delta C_p$, for the dissociation reaction is negligible over the experimental temperature range in the precise expression

$$\ln K_p = -\frac{\Delta H_0}{RT} + \frac{\Delta C_p}{R}\ln T + I \qquad (4)$$

where $\Delta H_0$ is the standard change in heat content for the dissociation reaction, $\Delta C_p$ is the difference in

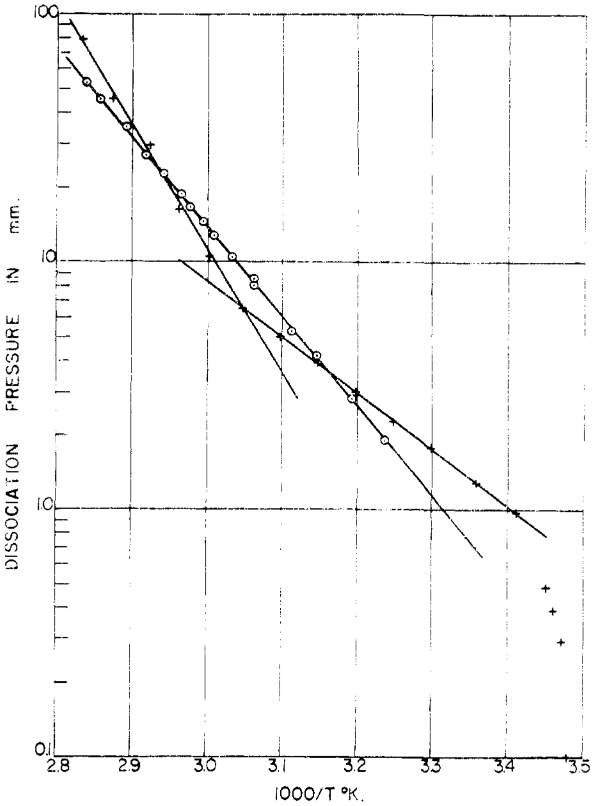

Fig. 2.—Comparison of dissociation pressure data for $KICl_4$: +, Caglioti and Centola; O, Smyth and Cutler.

heat capacities of the final and initial states at constant pressure, $I$ is a constant, and $K_p$ is the equilibrium constant for the reaction. If the heat capacity term is not negligible, a plot of log $p$ *vs.* $1/T$ will not be a straight line as is usually assumed.[5]

Using an estimated value of $-7.2$ cal./degree for $\Delta C_p$, values of $\Delta H_0$ and of $I$ have been evaluated using the dissociation pressures at the two temperatures where Caglioti and Centola's data cross ours, 43.2 and 67.2°, by relating $K_p$ to the observed total pressure over $KICl_4$ and the dissociation pressure of $KICl_2$ as given by Cornog and Bauer. Values of $K_p$ were then calculated from equation 4 for two intermediate temperatures, 58 and 80.5°, and compared with values obtained from the two sets of experimental data: calculated $K_p$, 16.3 and 251; from our data, 16.1 and 254; from the data of Caglioti and Centola, 10.7 and 386. A change in the estimated $\Delta C_p$ by a factor of two would change the calculated values of $K_p$ by less than 1%. It is apparent that the data of Caglioti and Centola deviate substantially from the calculated curve, and the curvature is in the opposite direction. It would require a $\Delta C_p$ of opposite sign and of much greater magnitude to fit their data. We feel, therefore, that our data more nearly represent the true values. It is interesting to note that our data for the dissociation pressure of $NH_4ICl_4$ show a small but distinct curvature in the direction required by the sign of the heat capacity term. It would be expected that the effect would be larger in the case of $NH_4ICl_4$ since its heat capacity should be larger than that of $KICl_4$ due to the more complex cation.

Caglioti and Centola state that the dissociation of $KICl_4$ proceeds directly to KCl without the formation of $KICl_2$ as an intermediate. They present three supporting arguments: (a) $ICl_3$ was observed as a condensed, solid phase under many experimental conditions, (b) a plot of weight loss *versus* time for the continuous dissociation of $KICl_4$ showed no abrupt change in the rate of dissociation, and (c) only KCl could be detected as a solid decomposition product by X-ray diffraction techniques. On the other hand it is difficult to see why $KICl_2$ is not formed as a decomposition product since its dissociation pressure is considerably less than half the total pressure over $KICl_4$. From thermodynamic considerations, even if the initial dissociation step were a complete breakdown to KCl and $ICl_3$, the $ICl_3$ would dissociate completely to $Cl_2$ and ICl and the latter should recombine with KCl to form $KICl_2$ until the ICl pressure is reduced to its equilibrium value over $KICl_2$.

The arguments offered in support of a one step dissociation by Caglioti and Centola can also be explained in terms of a two-step dissociation. Their observation of $ICl_3$ as a solid condensate from the dissociation of $KICl_4$ must have been made in an incompletely thermostated system. In our experiments no solid $ICl_3$ was noted unless the dissociation vapor had access to a surface appreciably cooler than the $KICl_4$. In such a case, $ICl_3$ was frequently observed to condense as would be expected considering the dissociation pressure of $ICl_3$ as given by Nies and Yost.[6] The requirement for condensation is that the temperature of some part of the system be such that $K_{p(ICl_3)} = p_{ICl}p_{Cl_2}$ is smaller than the value of $K_{p(KICl_4)} = p_{ICl}p_{Cl_2}$ at the $KICl_4$ temperature.

One would not expect an abrupt break in the rate at which $KICl_4$ loses weight since it is losing both $Cl_2$ and ICl at all temperatures and the rate should change only as the exposed surface areas change until all of the $Cl_2$ is finally lost. Actually the weight loss curve shown by Caglioti and Centola does show a gradual decrease in slope when the $KICl_4$ has lost about 75% of the total calculated weight loss and this may correspond to total depletion of chlorine.

The failure to observe $KICl_2$ as a decomposition residue by X-ray diffraction is probably due to the poor crystallinity of these materials. One would expect in particular that the solid dissociation products would be extremely finely divided and in a poorly crystalline state. We were able to obtain fair diffraction patterns from $KICl_4$, but a diffraction pattern obtained from $KICl_2$ showed no significant lines except those attributable to KCl. Thus it is not surprising that the diffraction pattern of partially dissociated $KICl_4$ reported by Caglioti and Centola showed only characteristics of $KICl_4$ and KCl.

We have obtained direct evidence of the formation of $KICl_2$ as an intermediate by measuring the e.m.f. of $Ag/AgCl/KICl_4$ cells as a function of the decomposition of the polyhalide. Two stable

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(5) S. Glasstone, "A Textbook of Physical Chemistry," 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 331.

(6) N. P. Nies and D. M. Yost, THIS JOURNAL, **57**, 306 (1935).

e.m.f.'s were observed: the initial value of 1.04 volts attributable to a $Ag/AgCl/Cl_2$ cell in which the $Cl_2$ is in equilibrium with $KICl_4$, and a subsequent value of 0.89 volt which was shown to be the e.m.f. of a Ag/AgCl/ICl cell in which the ICl is in equilibrium with $KICl_2$.

Thus it is shown that $KICl_4$ dissociates in the two steps shown in equations (2) and (3) with the greater part of the pressure being due to chlorine as can be seen by comparing the dissociation data of Cornog and Bauer for $KICl_2$ with our data for $KICl_4$.

The rate at which equilibrium was attained in the pressure measurements depended on the stability of the salt. $KICl_4$ and $NH_4ICl_4$ came to equilibrium in about one hour while it was necessary to allow a full day between pressure readings for the rubidium, cesium and tetramethylammonium salts. All of the data were taken in the direction of increasing temperature since equilibrium was attained very much more slowly in the direction of decreasing temperature. The $KICl_4$ system did appear to be reversible above 60°, but after cooling to 25°, pressures ten times greater than the equilibrium value were maintained for several days without change. This irreversible effect may be caused by the formation of a protective film over the KCl or $KICl_2$ by their initial recombination with ICl or $Cl_2$ as the temperature is reduced. This coating hinders the access of halogen to the underlying salt and thus delays further recombination. On the other hand, equilibrium is not hindered by decomposition since the finely divided solid dissociation products fall away from the $KICl_4$ and expose undissociated surface.

## Experimental

The tetrachloroiodide salts were prepared as described by Chattaway and Garton[7] by passing a stream of chlorine into a saturated aqueous solution of the appropriate iodide or into a saturated solution of the chloride to which slightly less than an equivalent of iodine has been added. A deliberate deficit of iodine was used to ensure the absence of $ICl_3$ which would give false vapor data. The chlorine stream was continued for about two hours after the liberated iodine or original iodine had redissolved. The solution was then cooled in ice-water and the yellow crystalline product separated by means of a suction filter. The tetrachloroiodide salts were vacuum dried over Drierite.

The $KICl_2$ was made by adding a slight deficit of triply recrystallized ICl to a saturated aqueous solution of KCl. The product was separated and dried as above.

The identities of the samples were determined by measuring their weight loss after complete thermal dissociation. Although the weight loss was generally less by 1–2% than the calculated loss for the pure salt, this test gave assurance that the salts were essentially the tetrachloroiodides and not dichloroiodides. The small discrepancy in weight loss is attributed to previous loss during the extensive vacuum drying period or to the use of excess chloride in the original preparation.

The salts were prepared from Baker and Adamson reagent grade potassium iodide, potassium chloride and ammonium iodide, Eastman tetramethylammonium iodide, Fisher purified rubidium chloride and cesium chloride, Matheson, Coleman and Bell reagent grade iodine and Matheson chlorine.

The dissociation vapor pressures were measured in an apparatus similar to that of Ephraim.[1] This consisted of a detachable sample section comprised of sample bulb, safety trap and null-balancing manometer. The design was such that the part of the apparatus containing the tetrachloroiodide and its equilibrium vapor was completely thermostated. This is necessary to avoid condensation of $ICl_3$ in the higher pressure regions.

Between each experimental run the detachable section was cleaned and dried at 110°. It was then attached to the main apparatus and the small null-indicating manometer was filled to a suitable level with Baker and Adamson reagent sulfuric acid. After introduction of the polyhalide salt, both sides of the apparatus were evacuated at about the same rate so that the sulfuric acid remained in approximate balance. The acid was outgassed by cautious flaming and the sample section was sealed off. After equilibrium had been attained at the desired temperature the dissociation pressure of the sample was balanced in the external apparatus by introduction or withdrawal of air. The balanced pressure was then read on a mercury manometer against a wooden meter stick whose slight scale misalignment was taken into account. The pressure readings are considered accurate to ±0.25 mm. Pressures were measured at 3–4° intervals up to about 80° after which the apparatus was cleaned and recharged. This procedure was necessary because equilibrium under conditions of decreasing temperature was not attained even after days.

The construction of the solid electrolyte cells will be described elsewhere. The e.m.f.'s of these cells were measured with a Keithley Vacuum Tube Electrometer, Model 210.

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The analyses by emission spectroscopy were performed by Dr. Robert Fellows and mathematical analysis of the data was carried out by Miss Kathryn Church.

NORTH ADAMS, MASS.

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[7] F. D. Chattaway and F. L. Garton, *J. Chem. Soc.*, **125**, 183 (1924).