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THE SOLUBILITY OF LEAD HALIDES

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THE SOLUBILITY OF LEAD HALIDES
IN DIOXANE WATER-MIXTURES

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INTRODUCTION

THERMODYNAMICS OF SOLUTIONS

The thermodynamic approach to a study of electrolytic solutions aims at determining the extent and direction of a chemical reaction by considering the energy changes which take place.

These energy changes may be measured experimentally from some property of the system thus giving thermodynamic functions without considering the mechanism of the solution process or alternately, by purely theoretical calculations based on a postulated model for the process. The validity of any theories connected with this latter aspect, which is a difficult and complicated one, are tested by their agreement with the former.

Hence any experimental study of a system such as the solubility of an electrolyte with which this work is concerned could, if accurate thermodynamic functions are obtained, supply a small contribution to the knowledge of a mechanism for such a reaction.

The energy (U) of a system can be expressed as a function of the variables, pressure (P), volume (V), temperature (T) and numbers of mols of each of the c components, $n_1, n_2, \ldots, n_c$, in the phase. The energy of a phase in terms of these
variables is
\[ U = f(P, V, T, n_1, n_2, \ldots, n_c) + U^0 \]
where \( U^0 \) is the energy in some arbitrary state.

The first law of thermodynamics requires that the increase in energy of a system equals the heat absorbed by the system plus the mechanical and electrical work done on the system by the surroundings. The second law requires that the reversible heat \( (q) \) absorbed by the system is \( dq = Tds \) where \( S \) is the entropy function.

The chemical potential \( (\mu) \) represents the rate of change in energy per mol of component - i.e.
\[ \mu_1 = \frac{\partial U}{\partial n_1}, \quad \mu_2 = \frac{\partial U}{\partial n_2} \quad \text{and so on.} \]
A generalised representation of the first and second laws then becomes for reversible processes
\[ du = Tds - PdV + \mu_1 dn_1 + \ldots + \mu_c dn_c \]

The extensive properties, heat content \( (H) \), work content \( (A) \), and free energy \( (G) \) are defined by the equations -
\[ H = U + PV, \quad A = U - TS, \quad G = H - TS. \]

Therefore
\[ \mu_1 = \left( \frac{\partial U}{\partial n_1} \right)_{S, V, n_2, \ldots, n_c} = \left( \frac{\partial H}{\partial n_1} \right)_{S, P, n_2, \ldots, n_c} = \left( \frac{\partial A}{\partial n_1} \right)_{V, T, n_2, \ldots, n_c} = \left( \frac{\partial G}{\partial n_1} \right)_{P, T, n_2, \ldots, n_c} \]
The bracketed terms are called partial molal quantities.
For systems at constant temperature and pressure any extensive property $X$ can be expressed as

$$dX = \sum_{i} \mu_{i} dn_{i} + \mu_{0} dn_{0} = \sum_{i} \mu_{i} dn_{i}$$

(A)

therefore

$$X = \mu_{1} n_{1} + \mu_{2} n_{2} + \ldots + \mu_{n} n_{n} = \sum_{i} \mu_{i} n_{i}$$

(B)

Complete differentiation of (B) yields the result

$$dX = \sum_{i} \mu_{i} dn_{i} + n_{i} d\mu_{i}$$

By combination of (B) with (A) the important Gibbs-Duhem equation is derived

$$\sum_{i} n_{i} d\mu_{i} = 0$$

The Activity of an Electrolyte

By the use of chemical potentials the thermodynamics of solutions have been developed. For the application of thermodynamics to this subject, however, it became necessary to introduce the activity function, the activity $(a_{i})$ of a pure chemical species or constituent of a solution being defined by the equation

$$\mu_{i} = \mu_{0}^{\circ} + RT \ln a_{i},$$

where $\mu_{i}^{\circ}$ is its chemical potential in some arbitrary standard state. This can now be expressed by its equivalent

$$\overline{\mu}_{i} = \overline{G}_{i}^{\circ} + RT \ln a_{i},$$

where $\overline{G}_{i}$ is the partial molal free energy of the constituent and $\overline{G}_{i}^{\circ}$ is its value in the standard state.

Although the actual ionic constituents are of fundamental importance in determining the properties of a system their concentrations are not independent variables so that chemical
potentials, free energies or activities of individual ionic species cannot be evaluated by thermodynamics. Nevertheless "hypothetical" ionic activities are often used although only ionic activity products have any real physical significance.

If an electrolyte $A_xB_y$ dissociates according to

$$A_xB_y \rightarrow xA^{+y} + yB^{-x}$$

then its activity may be written

$$a = a_x^a a_y^a = a_x^{(x+y)}$$

$a$ and $a_x$ are the individual activities of the ionic constituents while $a_x$ is termed the mean activity of the ions and hence

$$\bar{a} - \bar{a}^0 = (x + y)RT\ln a_x.$$ At constant temperature and pressure, from the Gibbs-Duhem equation $\sum n_i \ln a_i = 0$ where $n_i$ is the number of mols of component "i".

In solutions of such high dilution that the interaction between solute particles can be neglected it has been shown that the activities of solutes will approach their concentrations. On this basis the selected reference state is $\frac{a_x}{m_x} = f_x = 1$ at infinite dilution of the solvent. $m_x$ is the mean ionic concentration of the electrolyte. $f_x$ which describes the departure of real solutes from ideality is the activity coefficient or the mean ionic activity coefficient. If, however, an electrolyte is not completely dissociated into ions and $m_S$ is the total molality of the salt as determined by analysis $\frac{a_x}{m_S} = \gamma$, the stochiometric activity coefficient.

Then $\gamma = \frac{m_x f_x}{m_S} = \alpha f$ since $\frac{m_x}{m_S} = \alpha$ the degree of dissociation.
Consider the general reaction

\[ aA + bB + \ldots \longrightarrow lL + mM + \ldots \]

The change in free energy \( \Delta G = \sum n_i \mu_i \)

\[ = (L \mu_L + M \mu_M + \ldots) - (a \mu_A + b \mu_B + \ldots) \]

\[ = (L \mu_L + M \mu_M + \ldots) - (a \mu_A^0 + b \mu_B^0 + \ldots) \]

\[ + \frac{RT \ln a \mu^m_A \mu^m_L}{L \mu_M} \]

\[ a \mu^a_A \mu^b_B + \ldots \]

\[ = \Delta G^o + RT \ln a \mu \] where \( Q_a \), called the reaction constant represents the last term of equation (C). In the more important case of equilibrium where \( \Delta G = 0 \), \( \Delta G^o = -RT \ln K_a \), where \( K_a \) is the thermodynamic equilibrium constant for the reaction.

Using this equation other useful thermodynamic quantities can be evaluated by combining them by the first and second laws.

\[ \Delta S^o = -\frac{d}{dT} (\Delta G^o) \] and since \( \Delta G^o = \Delta H^o - T \Delta S^o \)

\[ \Delta H^o = \Delta G^o + T \frac{d}{dT} (\Delta G^o) \]

\( \Delta G^o, \Delta S^o, \Delta H^o \) are respectively the standard free energy, entropy and heat content.

The Process of Solution

By this process is meant the dissolving of a solid crystal \((MX)\) to give solvated ions.

\[ MX \rightarrow M^+ \text{ solvated} + X^- \text{ solvated} \]
This will be designated as process III and any thermodynamic functions connected with this process will have the subscript III as $\Delta G^0_\text{m}$ or $\Delta S^0_\text{m}$.

Methods for the Measurement of these Quantities

There are in general two approaches -

1. Measurement of $\Delta G^0_\text{m}$ as a function of temperature.
2. Free energies calculated from solubility and activity coefficient data are combined with heats of solution obtained calorimetrically to obtain entropy values.

It is with (1) that this laboratory has been concerned. One method of obtaining $\Delta G^0_\text{m}$ is to measure the E.M.F. of a reversible galvanic cell as a function of temperature. A suitable cell is of the type -

$$\begin{align*}
\text{Pb} & \quad \text{PbCl}_2\text{ saturated solution} & \text{AgCl(s)} & \quad \text{Ag} \\
\text{amalgam} & & & \\
\end{align*}$$

for which the E.M.F. can be formulated

$$E = E^0 - \frac{RT}{nF} \ln a_{\text{Pb}^{2+}} a_{\text{Cl}^-}$$

A value of $f_x$ can be obtained and consequently the activity product by extrapolation of $E$ to zero ionic strength.

Another method, the one used for this work involves a combination of solubility and activity coefficient data to evaluate the activity product. In the case of a divalent salt forming a saturated solution in a certain solvent $K_a$ is the thermodynamic solubility product and for a salt of
formula $MX_2$ assuming complete dissociation the reaction can be written $MX_2 \rightleftharpoons M^{+2} + 2X^-$, for which

$$K_a = \frac{aM^{+2}a^2X^-}{aMX_2}$$

$aMX_2$ is unity by convention.

If $m$ is the stochiometric molality of $MX_2$,

$$K_a = m \times (2m)^2 \times f_+ (f_-)^2$$

$$= 4(mf_+)^3$$

The solubility $m$ can be accurately obtained experimentally and several methods are available for obtaining $f_+$.  

1. **Vapour pressure measurement.** In this method it is necessary to measure the partial vapour pressure of the solute over a very dilute solution as well as that over the experimental solution. Since the former cannot be obtained with any accuracy the method is seldom used.

2. **Freezing Point lowering measurements.** The activity of the solute in the solution is determined at the freezing point of the solution so that the values must be corrected to the required temperatures. The method is capable of giving accurate results even in dilute solutions.

3. **Calculation of activity coefficients from equations derived from theoretical postulates.**

4. **The Lewis extrapolation or solubility method.** This method has been used extensively for saturated solutions of salts of low solubility. Lewis and Randall defined the ionic strength ($\mu$) of a solution by the equation $\mu = \frac{1}{2} \sum m_i z_i^2$, where $m_i$ and $z_i$ are
the molality and valence respectively of each species of ion present. It was established theoretically and empirically that \( \log f_+ \propto \sqrt{\mu} \) in dilute solutions. As \( f \to 1 \), that is in very dilute solutions \( \log f \propto f \) so that \( f \) becomes \( \propto \sqrt{\mu} \) and since \( (m_+ f_+) = (a_+) \), therefore \( f_+ \propto \frac{1}{m} \) and \( \frac{1}{m_+} \propto \sqrt{\mu} \)

By plotting values of \( \frac{1}{m} \) against \( \sqrt{\mu} \) a straight line should be obtained and as \( \mu \to 0 \), \( m^0 = a_+ \) since \( f_+ \to 1 \). Therefore

\[
\lim_{\mu \to 0} \left( \frac{1}{m} \right) = \frac{1}{m^0} = \frac{1}{a_+}
\]

By determining the solubility of the salt in the presence of varying amounts of added electrolyte, thus providing variation in the ionic strength and plotting \( \frac{1}{m} \) against \( \sqrt{\mu} \), on extrapolation to \( \sqrt{\mu} = 0 \), a value of \( \frac{1}{m^0} \) is obtained. Activity coefficients at desired molalities of the salt will then be found from the relation \( \frac{a_+}{m_+} = f_+ \).

**CALCULATION OF THE ACTIVITY COEFFICIENT**

Until 1923 the activity coefficient was regarded as an empirical quantity but due to the work of Debye and Hückel who took into account interionic forces it has become possible in some cases to calculate activity coefficients of ions in dilute solutions. The forces between ions, considered as point charges, are taken to be wholly coulombic and complete dissociation is assumed. Surrounding each ion there will be an oppositely charged ionic atmosphere so that dilution of a solution will
involve work against electrostatic attraction in addition to the free energy of dilution for an ideal solution which is determined only by the decrease of ionic concentration. The difference between actual and ideal free energy changes is a measure of the activity of the particular ion in a given solution. The final equation takes the form

$$-\log f_\pm = \frac{A z_+ z_- \sqrt{\mu}}{1 + B \sqrt{\mu}}$$

\(\mu\) is the stochiometric ionic strength; \(z_+\) and \(z_-\) are the valencies of the ions; \(A\) and \(B\) are constants depending on the dielectric constant of the medium and the temperature; \(a\) is the average distance of approach of two oppositely charged ions or the radius of the ion atmosphere.

In very dilute solutions the above equation reduces to

$$-\log f_\pm = Az_+ z_- \sqrt{\mu}$$

known as the Debye-Hückel limiting law. In many cases the application of these two equations has proved successful for dilute solutions.

This is not the case, however, for the lead halides and many other "intermediate" or "weak" electrolytes. An extension of the Debye-Hückel treatment involving the higher terms obtained from a more complete solution of the Poisson equation was made by Gronwall, La Mer, and Sandved who developed the equation for the symmetrical type of electrolyte and La Mer, Gronwall and Grief for the unsymmetrical type. For a 1-2 electrolyte their expression reduces to -
\[- \frac{\ln r}{2 \lambda_2^2} = \frac{1}{a} \left( \frac{10^6 e^2}{kT} \right)^{1/3} \frac{x}{1-x} + \frac{1}{a^2} \left( \frac{10^6 e^2}{kT} \right)^2 \left[ \frac{1}{3} x_2(x) - x_3(x) \right] \]

\[- \frac{2}{a^3} \left( \frac{10^6 e^2}{kT} \right)^3 \left[ \frac{1}{4} x_4^*(x) - 2x_3^*(x) \right] \]

\[- \frac{9}{a^6} \left( \frac{10^6 e^2}{kT} \right)^6 \left[ \frac{1}{2} x_7(x) - 2x_3(x) \right] \]

where \( x = aB \mu \) (\( a, B, \mu \) are identical with those used in the Debye treatment), and \( \left[ \frac{1}{3} x_2(x) - x_3(x) \right] \) etc. are functions of \( x \) tabulated by the two authors referred to above.

As a result of this equation, for electrolytes of high valence type whose \( a \) values are small, large departures from the Debye-Hückel approximation are to be expected even in a medium of high dielectric constant such as water but particularly in solvents of low dielectric constant. For a univalent electrolyte the Debye-Hückel treatment will apply if the mean ionic diameter is greater than about 1.5\( \text{Å} \) but for a bivalent salt the diameter must exceed 6\( \text{Å} \). In solvents of low dielectric constant, however the Gronwall-La Mer terms only become negligible if the diameters are larger than in water. Quantitative tests on this equation have shown it to be an improvement on the original one.

An alternative simpler method has been suggested by Bjerrum who appreciated the mathematical difficulties accompanying the complete solution of the Poisson equation.
By postulating the model that ions be considered as rigid unpolarisable spheres in a medium of fixed macroscopic dielectric constant, he considered the factors determining the extent of ionic association or more particularly the formation of ion pairs under the influence of coulombic forces. He then calculated a minimum value of the sum of the radii of two ions at which they can be considered as being associated in pairs. Similar to the above treatment the smaller the ions, the higher their valence and the lower the dielectric constant the more likely are the results to show deviation from the approximate treatment. If a minimum is $3.5A^0$ for a univalent salt in water at $25^\circ C.$ and if the sum of the ionic radii are smaller than this, there will be a tendency for ion pairs to form like $A^+ + B^- \rightleftharpoons A^+ B^-$, so that the electrolyte will be incompletely dissociated.

Extension of this idea of ion pairs was made by Fuoss and Kraus who considered the possibility of triple ions in addition to ion pairs in solvents of low dielectric constant as

\[ A^- B^+ + A^+ \rightleftharpoons A^+ B^- A^+ \]

or

\[ A^+ B^- + B^- \rightleftharpoons B^- A^+ B^- \]

As a result of this theory these workers derived theoretically an empirical rule concerning the minimum obtained in the equivalent conductance in solvents of very low dielectric constant. Bjerrum and Fuoss and Kraus derived equations whereby the dissociation constants of the ion complexes could be derived.
in terms of the dielectric constant and other physical constants. Several examples of the essential validity of this theory are known.

Another method of accounting for the incapability of the Debye-Hückel equation to explain the activity coefficients of "intermediate" type salts would be to assume incomplete dissociation and make some calculation of the degree of dissociation. The Debye-Hückel equation modified for this effect becomes

\[-\log f_+ = \frac{A_2z^2 \sqrt{\alpha a}}{1 + \text{Ba} \frac{1}{\sqrt{\alpha a}}}
\]

In this case the Lewis extrapolation method will be invalid as a determination of \(a_+\). A method to correct for incomplete dissociation in this treatment was suggested by Hogge and Garrett\(^5\).

In this connection the case of the lead halides is interesting as an example of the experimental techniques and theoretical methods which may be applied to all moderately strong electrolytes. In particular, studies have been made on the activities of lead chloride in water and the deviation of the behaviour of this salt from that of a strong electrolyte explained on the basis of the Gronwall-La Mer extension and on the basis of incomplete dissociation.

M.C. Hannan\(^6\) applied the former method to calculate the \(E^0\) of a galvanic cell containing a solution of lead chloride
in water. The results over the whole range of temperature were represented by a single value of the parameter $a = 1.75A^0$. Later it was suggested that the results may be treated in terms of ionic association to form one or more complexes. This interpretation is strengthened by the discovery of ultra-violet absorption bands identified with the PbCl$_{1}$ ion by Fromherz.$^7$

Thus PbCl$_{1}$ can be treated as incompletely dissociated, the only significant equilibrium being PbCl$_{1} \rightleftharpoons Pb^{2+} + Cl^-$. If $\alpha$ is the degree of dissociation for this reaction

$$\log \frac{Y}{\alpha} = \log f_\alpha = -A \sqrt{\frac{\alpha}{C}}$$

and it will have a dissociation constant $K$.

This approach had been suggested a short time before by Righellato and Davies$^8$ to explain the anomalous conductance of lead chloride solutions which along with other "weak" electrolytes did not obey the usual equation for equivalent conductance. Assuming the conductance to be the sum of the conductances of Pb$^{2+}$, Cl$^-$ and PbCl$_{1}$ ions, they determined the degree of dissociation $\beta$ required to yield the observed conductance. Ionic concentrations are then $mPb^{2+} = (1 - \beta)m$, $mCl^- = (2 - \beta)m$ and $mPbCl^+_1 = \beta m$ so that the actual ionic strength is $\mu' = (3 - 2\beta)m$. This differs from $\mu = 3$, the stoichiometric value, which is the actual ionic strength in a solution of a strong electrolyte. The value of $\beta$ was determined by successive approximation, the thermodynamic dissociation constant was calculated to be $0.0304$ at $18^0C$. and the value
of \( \gamma \), calculated from the Debye-Hückel equation gave \( a = 6.66 \text{Å} \)
considerably larger than the sum of the crystal radii (2.75Å),
but more plausible than 1.75Å required by the other method.

Garrels and Gucker\(^9\) measured the E.M.F. of cells contain­
ing lead chloride in the presence of other electrolytes. It
was found that their data and that of other workers could be
correlated by assuming a secondary dissociation constant (K)
of .03, calculating the ionic concentrations and plotting a
suitably defined function against actual ionic strength. These
results therefore show excellent agreement with the conductance
data of Righellato and Davies but wide divergence from that
calculated by Fromherz (K = .0775 at 25°C.).

Because of this large disagreement between the two values
of K Garrels and Gucker attempted to evaluate it independently
from E.M.F. data. They used the method described by Scatchard
and Teft\(^{10}\) and modified by Harned and Fitzgerald\(^{11}\) who assumed the
dissociation for cadmium chloride in aqueous solution to be
\[ \text{CdCl}_2 \rightarrow \text{Cl}^- + \text{CdCl}^+ \rightleftharpoons \text{Cd}^{2+} + \text{Cl}^- \].
A method was
developed for calculating \( \alpha \) and K and hence real activity
coefficients and actual ionic concentrations by successive approxi­
mations using arbitrary values of K. When applied to the lead
chloride case a value of K was found similar to the one obtained
from conductance and from this E\(^0\) values were calculated which
were about midway between those of the direct linear extrapola­
tion against \( \sqrt{\mu} \) and the extended La Mer-Gronwall theory.
Fromherz also obtained evidence of a complex ion of type $\text{PbX}^+$ in lead bromide and iodide solutions for which the dissociation constants were 0.071 and 0.0345 respectively. Hence similar treatment will be required for these two halides as for lead chloride.

The calculation of the activity coefficients of the lead halides is then a complicated problem and the methods outlined here are probably only very approximate and semi-empirical.

**THEORETICAL THERMODYNAMIC FUNCTIONS**

It is useful to consider the process of solution of a crystal $MX(s)$ as made up of three steps -

\[ MX_s \xrightarrow{I} M^+(g) + X^-(g) \]

\[ \xrightarrow{II} \quad \text{M}^+ \text{solvated} + X^- \text{solvated} \]

Process I describes the change solid salt $\rightarrow$ gaseous ions and is called "sublimation". Process II describes the change gaseous ions $\rightarrow$ ions in solution or solvated ions and is called "solvation". Process III which is the sum of these two processes describes the change solid salt $\rightarrow$ ions in solution and is called the process of solution.

Any thermodynamic function $X$ of these processes may, by the first law be added algebraically i.e. $\Delta X = \Delta X_1 + \Delta X_2$. 
It is with the process of solvation that many theories are concerned and thermodynamic functions calculated from them may be compared with those measured experimentally for this process.

$$\Delta H^0 = \Delta H^0_{\text{HI}} - \Delta H^0_{\text{IT}}$$

$\Delta H^0_{\text{HI}}$ is measurable and $\Delta H^0_{\text{IT}}$ is identical with the lattice energy which is known for most salts.

Also

$$\Delta S^0 = \Delta S^0_{\text{HI}} - \Delta S^0_{\text{IT}}$$

$\Delta S^0_{\text{HI}}$ is measurable and $\Delta S^0_{\text{IT}}$ which =

$$\left[ \sum S^0 \text{ions in solution} - \sum S^0 \text{gaseous ions} \right]$$

can be calculated. $\sum S^0$ are the standard partial molal entropies of the ions in solution while $\sum S^0$ are the standard entropies of those ions in the gaseous state.

$\sum S^0 \text{ions in solution} = \Delta S^0_{\text{HI}} + S^0_{\text{MX}}$

$S^0_{\text{MX}}$, representing the entropy of the solid salt can be calculated from heat capacity data on the assumption of the third law of thermodynamics. $\sum S^0$ gaseous ions can be calculated from the Sackur-Tetrode equation derived by the statistical mechanics method. This equation for one mol of a gaseous ion is

$$S^0_{\text{ion}}(g) = \frac{3}{2} \text{Rln} M + 26.00$$

where $M$ is the atomic weight of the ion. A correction must be applied to this equation to transfer it from the standard state of the gas to the standard state of the solution. The complete equation for the entropy of solvation is therefore

$$\Delta S^0 = \Delta S^0_{\text{HI}} + S^0_{\text{MX}} - \left[ \sum S^0 \text{gaseous ions} - n\text{Rln } 24.46d \right]$$

where $d$ is the density of the solvent and $n$ is the number of ions formed.
From $\Delta H^0_{\text{fH}}$ and $\Delta S^0_{\text{fH}}$ the free energy of solvation can be obtained from

$$\Delta G^0_{\text{fH}} = \Delta H^0_{\text{fH}} - T\Delta S^0_{\text{fH}}$$

Theoretical Functions

The Debye-Huckel theory has already been discussed.

The Born Theory By assuming that the work done in introducing a gaseous ion into solution is due only to the transfer of a charged sphere from air into a medium of continuous dielectric constant, Born\textsuperscript{12} was able to formulate an expression for the free energy of solvation. The work required to charge a sphere of radius $r$ and valence $z$ in a medium of dielectric constant $D$ is

$$W = \frac{(ze)^2}{2Dr} \text{ per ion where } e \text{ is the charge on the ion.}$$

Therefore the work of transferring an ion from air ($D = 1$) to a medium of dielectric constant $D$ is

$$W = \frac{(ze)^2}{2r} (1 - \frac{1}{D}) \text{ per ion}$$

therefore

$$-\Delta G^0_{\text{fH}}(\text{B.C.)} = \frac{N}{2r} \frac{(ze)^2}{2r} (1 - \frac{1}{D}) \text{ per mol}$$

This process is often called "Born charging" (B.C.).

The entropy $\Delta S^0_{\text{fH}}(\text{B.C.)} = -\frac{d}{dT} (\Delta G^0_{\text{fH}}(\text{B.C.)})$

$$= \frac{N(ze)^2}{2r} \frac{1}{D^2} \frac{dD}{dT}$$

The two uncertain terms of this equation are $r$ and $D$. The term required for $D$ is not the dielectric constant of the solvent but the dielectric constant in the immediate neighbourhood of the ion. The correct value is still an
unsolved problem. For \( r \), at first crystallographic radii were used but they gave poor agreement with experiment. Latimer, Pitzer and Slansky\(^1\) found that if \( .85A^0 \) and \( .10A^0 \) were added to the radii of positive and negative ions respectively much better agreement was obtained. It is the radius of the cavity in the solvent where the ion is situated that is required and this will be greater than the crystallographic radius and will be greater for the cation than the anion. The above correction is, however, only an empirical one.

Dunning and Shutt\(^1\) derived directly from the Born equation an expression relating the solubility of a salt \( A_xB_y \) in two solvents of uniform dielectric constant \( D_A \) and \( D_B \):

\[
\frac{x^2 + y^2}{2r} \epsilon \left( \frac{1}{D_A} - \frac{1}{D_B} \right) + (x + y) kT \ln \frac{C_A}{C_B} = 0
\]

where \( k \) is the Boltzmann constant and \( C_A \) and \( C_B \) are the concentrations of \( A_xB_y \) in saturated solutions of solvents in mols per litre since Bell and Gatti\(^1\) found this concentration scale to be the most accurate. A plot of \( \log C \) against \( \frac{1}{D} \) will be linear if this relation holds.

If solubilities are known \( r \) can be calculated by this equation as a mean radius between \( D_A \) and \( D_B \) and values of \( r \) can then be interpolated for the actual solvents used. If it can be assumed that \( a = 2r \) it would be possible to use this value of \( a \) to calculate activity coefficients by the Gronwall-
La Mer extension discussed previously.

Ricci and Davis Theory  From the empirical observation that for many slightly soluble electrolytes the activity coefficients in saturated solutions of pure solvents are almost constant and independent of the dielectric constants, Ricci and Davis\textsuperscript{16} deduced the equation -

$$\log m_2 - \log m_1 = 3 (\log D_2 - \log D_1)$$

from which a plot of $\log m$ against $\log D$ should be linear with gradient $= 3$. Since in many cases their assumption is not justified the theory is not a very useful one.
EXPERIMENTAL

OUTLINE OF THE WORK

This work has been concerned with the determination of the solubility of lead chloride, bromide and iodide in mixed solvents of dioxane and water over a temperature range 25°C to 45°C.

The results have been used to test the Born theory and have been discussed in reference to special aspects of the solubility of salts in media of low dielectric constant.
PREPARATION AND PURIFICATION OF MATERIALS

LEAD HALIDES

These salts were prepared by precipitation reactions in dilute solutions and were recrystallised from slightly acid solutions as recommended by Baxter and Grover who showed that appreciable hydrolysis to a basic chloride takes place in neutral solutions. The salts were dried under vacuum and over solid potassium hydroxide for 14 days when they were pulverised and replaced. The bromide and iodide were stored in darkened bottles due to their photosensitive properties. Before use small quantities were heated in an electric oven at 100°C for one hour.

Lead Chloride

Lead nitrate and sodium chloride (Hopkin and Williams "AnalaR") were weighed out in molecular proportions to give 100g of lead chloride. The former dissolved in 1 litre of water was added slowly to 500ml sodium chloride in 0.018 N HCl (A.R.). The flask was stood in the dark with occasional shaking for several days. The precipitate was then washed six times by decantation from ice-cold 0.006 N HCl and transferred to a Buchner funnel and thoroughly washed and drained.

The lead chloride was then recrystallised three times from boiling 0.006 N HCl and shocked cooled to obtain small sized particles. The mother liquor from each recrystallisation
was evaporated down to improve the otherwise low yields of crystals.

**Lead Iodide**

Lead iodide was prepared in a similar way to lead chloride from lead nitrate and potassium iodide. 0.001 N acetic acid was used to prevent hydrolysis. Only one recrystallisation from dilute acetic acid was carried out since the low solubility of 5g. per litre at 100°C made the process very tedious.

**Lead Bromide**

One litre hydrobromic acid (H and W. Density 1.46 - 1.49) was diluted with water to give a percentage composition below that of the constant boiling mixture and was twice distilled through a fractionating column packed with glass beads. Before distillation carbon dioxide was blown through the apparatus to produce a reducing atmosphere. The constant boiling solution at 126°C which was colourless was collected and the first and last fractions coloured yellow and red respectively were discarded. 0.01N HBr was then prepared by dilution.

The lead bromide was precipitated from lead nitrate solution and sodium bromide in 0.01N HBr at 60°C. Instead of carrying out the process of recrystallisation from 0.01N HBr the method of Baxter and Thorvaldson21, utilising the soluble complex formed between lead bromide and concentrated HBr and
decomposition of this complex on dilution, was used.

The precipitate was dissolved in 100c.c. of hot constant boiling HBr in a large silica dish and reprecipitation brought about by dilution with cold water. Three such recrystallisations were carried out and a final one from .01N HBr.

Analysis of these salts gravimetrically for lead as lead chromate gave the following results:

<table>
<thead>
<tr>
<th>Salts</th>
<th>% Pb Experimental</th>
<th>% Pb Theoretical</th>
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<tr>
<td>PbCl₂</td>
<td>74.49</td>
<td>74.50</td>
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<tr>
<td>PbI₂</td>
<td>44.94</td>
<td>44.94</td>
</tr>
<tr>
<td>PbBr₂</td>
<td>56.40</td>
<td>56.45</td>
</tr>
</tbody>
</table>

**SILVER NITRATE**

Silver nitrate (Hopkin and Williams recryst.) was used to make five litres of .01N solution and three litres of .08N solution. .01 and .08N potassium bromide solutions were made up accurately by weight and weighed amounts used for standardising the silver nitrate solutions using the adsorption indicator dichloro-R-fluorescein and by potentiometric titration. The silver nitrate solutions were stored in darkened bottles and their normalities were checked periodically throughout the course of the work.

**ADSORPTION INDICATOR**

0.1g. of dichloro-R-fluorescein was dissolved in 100ml. of 40% ethyl alcohol solution.
DITHIZONE

The commercial reagent was purified by dissolving 1g. in 50ml. chloroform and extracting with 1% ammonia solution in a separatory funnel in successive portions of 75ml. The ammoniacal extracts were combined, acidified with HCl and extracted with chloroform. Finally the dithizone was recovered by evaporation and drying at less than 50°C. Fresh solutions of dithizone in chloroform were made up when required.

DIOXANE

Commercial dioxane was purified by the method of Eigenberger. Two and a half litre amounts were refluxed for two days with 10% of NHCl to decompose ethylene acetal and at the same time a slow stream of air from an air-blower was passed through the condenser to facilitate the removal of acetaldehyde. By this method a complete separation was effected. The liquid was then treated several times with solid potassium hydroxide, the aqueous layer being removed by a separating funnel. After drying over sodium wire for several days it was fractionally distilled twice over metallic sodium and the middle fraction collected at approximately 101.3°C. Before each distillation the dioxane was refluxed for a short time until the sodium assumed a bright lustre like mercury showing that no further reaction with water was taking place. The final product a colourless pungent smelling liquid was stored in carefully dried Winchester stoppered
with corks wrapped in tin foil.

Density at 20°C. 1.0335 1.03326 (Weissberger and Proskauer\textsuperscript{33})

DIOXANE-WATER MIXTURES

These were prepared by weight dilution of dioxane with distilled water. In order to avoid unnecessary contamination with the atmosphere approximate concentrations were made up and actual concentrations subsequently calculated from the weights used.
APPARATUS AND PROCEDURE

Solubility bottles holding about 120ml. of solution were made from glass tubing. Excess of the lead salt was introduced into the bottles and thoroughly washed with the appropriate solvent. About 100ml. of the solvent was then added and the bottles sealed in a blow-pipe, cotton wool plugs being used to prevent diffusion during the time between filling and sealing.

The bottles were clamped to a rotary shaker in a large thermostat and rotated headlong at the required temperature - 14 days at 25°, and 9 days at 35° and 45°. The temperature was held constant to ± 0.05° successively at 25°, 35° and 45° by a mercury toluene regulator controlling the supply of gas to the burner heating the bath. The thermometer (0-50°C) was calibrated against the laboratory M.P.L. standard. The bath was also fitted with an electric immersion heater, stirrer and constant level device.

After equilibration, each bottle was unclamped and placed on a stand on one side of the thermostat with its neck only above the surface. After leaving at least an hour for sedimentation the bottles were opened by filing a groove in the neck and applying a piece of heated glass tubing. Approximately 20ml. aliquots for the more concentrated solutions and up to 40ml. for the very dilute were withdrawn through
pipettes to each of which was attached by a short piece of rubber tubing, a small piece of glass tubing containing a plug of cotton wool. This acted as a filter. The solutions were delivered into previously weighed 50ml conical flasks which were corked and reweighed. In order to avoid crystallisation on withdrawal the pipettes and attached filters were previously heated to 60-70°C. Also before the initial weighing the appropriate amount of the strong electrolyte used in the analysis was added to the titration flask to prevent crystallisation of the lead salt on cooling. Four samples were taken from each solubility bottle the first of which was used only for obtaining a rough estimate of the solubility.

It was found convenient to divide the determinations into groups of 6 or 9 at each temperature according to the time required for equilibrium to be reached. Thus as soon as one group of bottles was unclamped they were replaced by the next group which was ready on completion of the first set of analysis. Any solution whose analysis required repetition was added to the group at that time in the thermostat.

Due to compound formation in the lead iodide solutions it was thought necessary to use fresh solid and solvent at each temperature.
THE ESTIMATION OF THE LEAD HALIDES IN DILUTE SOLUTION

The concentration range, 0.0567 - 0.000019 mols lead halide per 1000g. of solvent presents some difficulty when choosing an accurate method of analysis.

The adsorption indicator, dichloro-R-fluorescein was shown by Kolthoff, Lauer and Sunde\textsuperscript{24} to be suitable for the analysis of dilute halide solutions but this method was not investigated since Hamann\textsuperscript{25} and Smith\textsuperscript{26} had found it unsatisfactory at any high dilution. Also, lead iodide solutions in dioxane are coloured making any such method inapplicable. Use was made of this indicator, however, for suitable chloride and bromide solutions for gaining an approximate idea of the end point.

The differential potentiometric titration was used by Smith for concentrations down to 0.0002 molal lead iodide, while colourimetric analysis for lead by dithizone is said by Scott\textsuperscript{27} to be applicable from 2mg. lead (0.00005 molal lead halide) to 0.0001mg. lead. The latter method is described in detail by Craig and Vinal\textsuperscript{28} where it was successfully used over the range 0.000022 to 0.000002 mols of lead sulphate per litre of water.

Modifications of these two methods were used to obtain all the solubility data of this work.
1. **Differential Potentiometric Titration**

This method which was introduced by Cox\(^2^9\) and developed by MacInnes\(^3^0\) and co-workers is claimed to be simpler and more accurate than the ordinary electromeric titrations for the following reasons -

(a) Plotting of curves is eliminated

(b) The troublesome calomel half cell is avoided and hence errors due to liquid junction potential

(c) Slight errors due to "drifting" are compensated

(d) Since solutions are identical in composition all trouble from diffusion is avoided.

The measured difference in potential is developed between two similar electrodes when a small portion of the solution, separated from the bulk solution by some mechanical device, is withheld from reacting with the titrant. On equalising the concentrations the E.M.F. falls to zero. As the end-point is approached the potential difference observed on addition of each portion of titrant increases rapidly and finally shows a maximum at the stochiometric end-point. The variety in the apparatus is concerned mainly with the devices used for separating the solution around one of the electrodes. Among the simplest of these, the one adopted here, is that invented by Hall, Jensen and Baeckstrom\(^3^1\).

Platinum gauze electrodes were first silver plated from a solution of platinum silver cyanide, stood in concentrated ammonia to remove cyanide and washed in distilled water.
Ag/AgCl and Ag/AgBr electrodes were then prepared by making them the anode in .1N HCl or HBr. For Ag/AgI electrodes the method of Jones and Hartmann32 was followed using potassium iodide solution. The cell consisted of a 600ml. beaker containing the solution for analysis. One electrode was directly immersed into this solution while the other was enclosed in a tube to the bottom of which a short piece of capillary was joined. By means of this contact was made with the bulk solution. By operating a rubber bulb attached to a side arm of the tube, solution to cover the electrode could be drawn up or released as required.

A 10ml. microburette graduated to .05ml. was calibrated for each .5ml. increment and the drop size reduced to .01ml. by paraffining the tip. A mechanical stirrer run at a slow, steady speed was necessary for mixing and for maintaining a constant E.M.F.

Since differences of potential only were to be measured deflections read on a high resistance spot galvanometer (Instrument number C.13) connected across the cell in series with a .2 megohm variable radio resistance proved very satisfactory. To insure that the internal resistance of the cell remained constant an excess of a suitable strong electrolyte was added. For this purpose about 10ml. of .5N "AnalaR" nitric acid per sample for analysis as used by Smith was found satisfactory.
Procedure  The solution for analysis containing the nitric acid was transferred from the weighed flask to the beaker with the least amount of washings possible. If an approximate estimate of the volume of silver nitrate required had previously been made by the adsorption indicator method it was necessary to begin taking readings only in the neighbourhood of this value. The addition of a drop (0.01 ml.) of silver nitrate resulted in an E.M.F. due to difference in halide concentration around the two electrodes. Before the next addition of 0.01 ml. silver nitrate the concentrations were equalised by operation of the bulb and thorough mixing. This was continued until a maximum deflection on the galvanometer had been clearly detected. The reading on the burette at the maximum was taken as the equivalence point.

Results  The E.M.F.s at the end points were in accord with the theoretical equation of Lange and Schwartz\(^3\) who calculated that the E.M.F. at the maximum was given by the equation

\[
\Delta E_{\text{max.}} = \frac{RT}{F} \left( \frac{p}{2V/L} \right)
\]

where

- \(P = \) the number of equivalents of titrant added at each increment.
- \(L = \) the solubility product of the precipitated salt.
- \(V = \) the volume of the solution in litres.

The maximum was far less definite and easily determined for the chloride titrations than for the bromide and iodide as illustrated by the typical plots for chloride and bromide shown.
GRAPH I

ΔPbCl₂ solutions

ΔPbBr₂ solutions

Galvanometer Deflections

Drops of 0.00991 M AgNO₃ (1 drop = 0.01 ml)
in Graph I, A and B. This would be due to the lower solubility products of AgBr and AgI.

It was found essential especially for the chloride and bromide titrations to have clean well plated electrodes otherwise potentials were set up which gave either erroneous or double end-points.

In most cases the variation in titre did not exceed .02ml. per 10g. of solution, an accuracy of one part in five hundred.

The method was used for concentrations down to .0001 molal for which about 40ml. of solution were used. Values for concentrations as low as this were in good agreement with those obtained by method 2. below where a very small quantity of solution was taken in order to keep in the correct solubility range.

2. Colourimetric Analysis with Dithizone

Dissolved in an organic solvent such as chloroform or carbon tetrachloride dithizone (diphenylthiocarbazone) produces a green colouration but in the presence of small quantities of lead a bright cherry red lead dithizone complex is obtained and hence forms a means of colourimetric determination of concentration. The reaction is conveniently carried out in a two-phase system, one phase being an aqueous solution of pH greater than seven and the second an organic liquid immiscible with water. Ammonia solution and chloroform which are suitable for
these phases were used for this work.

The interference of other metals is inhibited by the addition of potassium cyanide and aluminium ions which may be present in the distilled water are retained in the ammoniacal solution by the addition of citric acid.

The "Spekker" photoelectric absorptiometer was the instrument used to measure the intensity of the colour. In this instrument which is quick and easy to use a photoelectric cell receives the radiation transmitted by the solution when exposed to a light source and the response of the cell is measured on a high resistance spot galvanometer (Instrument number C 13.)

Procedure A calibration curve was first constructed by taking readings with a number of coloured solutions of known concentration covering the required range. For this 20ml. aliquots were taken of accurately known lead nitrate ("AnalaR") solutions prepared by weight dilution of a more concentrated one. The plot of readings against concentration was approximately linear and was the steepest when orange filters controlled the range of wave lengths transmitted to the cell.

A weighed amount, about 20ml. or less, of each unknown was slowly evaporated to dryness in a silica dish since the dioxane would have interfered with the determination. 4ml. of concentrated nitric acid ("AnalaR") was added to the residue, then
10ml. of distilled water and the solution transferred to a separatory funnel the dish being rinsed twice with 0.3 ml. nitric acid followed by 10ml. water and finally with small quantities of water. The separatory funnel then contained about 40ml. water and 1ml. nitric acid. To this solution was added 2g. citric acid (free from lead), 3 ml. concentrated ammonia and 0.5ml. potassium cyanide solution (20g. in 100ml. water). A solution of 1g. dithizone in 300ml. chloroform was then added in successive small portions. The addition of each portion was followed by shaking and the process repeated until the additions of dithizone were sufficient to cause a visual change in colour of the chloroform solution from cherry red to a purplish red which indicated that a slight excess of the reagent had been added. For the removal of this excess the method described by Snell was followed. The chloroform layer was drawn off and shaken with 30ml. of an aqueous solution containing potassium cyanide, citric acid and 0.5ml. concentrated ammonia. Free dithizone is soluble in aqueous ammonia solutions producing a yellow colour. The chloroform layer was drawn off and the process repeated, usually twice, until the extracting solution was substantially colourless. The concentration was then determined by noting the response of the cell with the coloured chloroform solution and referring to the calibration curve.

Results Very few of the solutions were dilute enough to give satisfactory and reproducible results and where such small
quantities as 4 grams of solution were taken for analysis the accuracy was considerably lowered. However for those analyses below .00008 molal and for those between .00008 and .00012 which were determined also by the potentiometric technique the method proved useful.
CALCULATION OF RESULTS

Solubility

\[ m = \text{mols Pb halide per 1000g. solvent.} \]
\[ z = \text{ml. of } y \text{ N AgNO}_3 \text{ required in the titration.} \]
\[ w = \text{g. of solution.} \]
\[ M = \text{molecular weight of the Pb halide.} \]

Then the number of g. of Pb halide in wg. of solution

\[ = \frac{zy}{2000} M \]

Hence number of g. of solvent in wg. of solution

\[ = w - \frac{zyM}{2000} \]

Therefore

\[ m = \frac{zyM 1000}{2000M} \left( w - \frac{zyM}{2000} \right) = \frac{zy}{2} \left( w - \frac{zyM}{2000} \right) \]

These results are listed in Tables I, II and III together with the dielectric constants of the solvents interpolated from the values of Akerlof and Short.

In graphs II, III and IV the variation of solubility with increasing dioxane content of the solvent is shown as a plot of \( \log m \) against mol percentage dioxane for the three salts at each temperature.

In graph V \( \log m \) is plotted against the reciprocal of the dielectric constant as a test of the Born Theory.

Values of the Born radii for the three salts at 25°C. were calculated by the equation -
\[
r = \frac{5e^2}{3 \times 2.303 \times 2kT} \left( \frac{1}{D_A} - \frac{1}{D_B} \right) \log \frac{m_{1d}}{m_{2d}} \\
\]
\[e = 4.802 \times 10^{-10} \text{ e.s.u. and } k = 1.378 \times 10^{-16}.
\]
d = density of the solvent interpolated from Hovorka et alia\(^3\)\(^6\).

The results are shown in Table IV A.

Assuming the value of \(r = 5A^0\) in all the solvents, activity coefficients \(\gamma_i\) have been calculated at 25° C. from the equation:

\[- \log \gamma_i = \frac{A}{1 + B \left( \frac{\mu_i}{\mu_0} \right)}\]

where \(\mu_0 = 3m\)

and \(A = 1.8245 \times 10^6\)

\(B = 50.2904 \times 10^7\)

\(\frac{(DT)^2}{(DT)^3}\)

Thermodynamic solubility products and \(\Delta G_m^0\) were then calculated by the relations -

\[K_a = 4(m \gamma_i)^3\]

and

\[\Delta G_m^0 = -RT\ln K_a\]

These values are listed in Table IV B.
### TABLE I

**LEAD CHLORIDE**

- **m** = solubility in mols PbCl₂/1000g. solvent
- **D** = dielectric constant of the solvent
- **φ** = mols percentage dioxane in solvent

**Observations at 25°C.**

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<th>m</th>
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**Observations at 35°C.**

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### Observations at 45°C.

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GRAPH II

Solubility of Lead Chloride

Temperature (°C):
- 45°C
- 35°C
- 25°C

Mol. % Dioxane →

Log m →


TABLE II

LEAD BROMIDE

Observations at 25°C.

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<th>m</th>
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</tr>
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Observations at 35°C.

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Observations at 45°C.

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GRAPH III

Solubility of Lead Bromide
### TABLE III

**LEAD IODIDE**

#### Observations at 25°C.

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#### Observations at 35°C.

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#### Observations at 45°C.

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<tr>
<td>0.00</td>
<td>71.42</td>
<td>0.002916</td>
<td>3.4648</td>
</tr>
<tr>
<td>20.00</td>
<td>26.70</td>
<td>0.00184</td>
<td>3.2657</td>
</tr>
<tr>
<td>40.02</td>
<td>11.76</td>
<td>0.00174</td>
<td>3.2420</td>
</tr>
<tr>
<td>59.99</td>
<td>6.00</td>
<td>0.000895</td>
<td>4.9518</td>
</tr>
<tr>
<td>80.05</td>
<td>3.48</td>
<td>0.000404</td>
<td>4.6064</td>
</tr>
<tr>
<td>100.00</td>
<td>2.097</td>
<td>4.3784</td>
<td></td>
</tr>
</tbody>
</table>
GRAPH IV

Solubility of Lead Iodide

\[ \log m \]

Mol. % Dioxane ->
### TABLE IV

#### A. BORN RADII (r) AT 25°C.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Mean D</th>
<th>PbCl₂</th>
<th>PbBr₂</th>
<th>PbI₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-20</td>
<td>54.40</td>
<td>4.39</td>
<td>5.67</td>
<td>11.15</td>
</tr>
<tr>
<td>20-40</td>
<td>21.66</td>
<td>15.18</td>
<td>38.79</td>
<td>33.09</td>
</tr>
<tr>
<td>40-60</td>
<td>9.80</td>
<td>46.76</td>
<td>78.03</td>
<td>95.01</td>
</tr>
<tr>
<td>60-80</td>
<td>5.08</td>
<td>77.41</td>
<td>65.91</td>
<td>66.36</td>
</tr>
<tr>
<td>80-100</td>
<td>2.87</td>
<td>36.12</td>
<td>43.80</td>
<td>23.63</td>
</tr>
</tbody>
</table>

#### B. THERMODYNAMIC FUNCTIONS AT 25°C.

**Lead Chloride**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Ye</th>
<th>Kₐ</th>
<th>G (cals)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.348</td>
<td>1.37 x 10⁻⁸</td>
<td>10,730</td>
</tr>
<tr>
<td>40</td>
<td>0.145</td>
<td>1.79 x 10⁻¹¹</td>
<td>14,670</td>
</tr>
<tr>
<td>60</td>
<td>0.024</td>
<td>7.85 x 10⁻¹⁵</td>
<td>19,240</td>
</tr>
<tr>
<td>80</td>
<td>1.000 x 10⁻⁸</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Lead Bromide**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Ye</th>
<th>Kₐ</th>
<th>G (cals)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.331</td>
<td>2.67 x 10⁻⁶</td>
<td>7,603</td>
</tr>
<tr>
<td>40</td>
<td>0.052</td>
<td>1.24 x 10⁻¹¹</td>
<td>14,880</td>
</tr>
<tr>
<td>60</td>
<td>0.001</td>
<td>5.26 x 10⁻¹⁷</td>
<td>22,200</td>
</tr>
<tr>
<td>80</td>
<td>2.81 x 10⁻⁶</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Lead Iodide**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Ye</th>
<th>Kₐ</th>
<th>G (cals)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.514</td>
<td>1.69 x 10⁻¹⁰</td>
<td>13,290</td>
</tr>
<tr>
<td>40</td>
<td>0.326</td>
<td>1.70 x 10⁻¹²</td>
<td>16,070</td>
</tr>
<tr>
<td>60</td>
<td>0.073</td>
<td>6.2 x 10⁻¹⁵</td>
<td>19,380</td>
</tr>
<tr>
<td>80</td>
<td>0.018</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
GRAPH V

1. \[ \log_{10} m \uparrow \]

2. \[ \log_{\omega} m \uparrow \]

3. \[ V_D \rightarrow \]

\[ \text{PbCl}_2 \]

\[ \text{PbBr}_2 \]

\[ \text{PbI}_2 \]
DISCUSSION

A differential potentiometric technique gave good results over almost the whole solubility range and for all three halides. The colourimetric method of Craig and Vinal using the "Spekker" absorptiometer gave reasonably accurate values for the very low concentrations. This method, however, would be better applied to an even lower concentration range using purer materials and Pyrex glassware as these workers found ordinary glass unsatisfactory.

Noble and Garrett\(^3\) estimated the solubility of lead chloride in weight percentage dioxane mixtures at 25°C. using a gravimetric or colourimetric method of analysis. In order to effect a comparison with the present work their values were interpolated from weight percentage dioxane to the relevant mol percentage.

<table>
<thead>
<tr>
<th>Mol % Dioxane</th>
<th>Solubility in mols/1000g. solvent</th>
<th>Noble and Garrett</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.03905</td>
<td>0.03908</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.00435</td>
<td>0.00434</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.00143</td>
<td>0.00114</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0.00520</td>
<td>0.00529</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>0.00250</td>
<td>0.00254</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0.000013</td>
<td>0.000019</td>
<td></td>
</tr>
</tbody>
</table>

The value in 40% dioxane which differs appreciably from that
of Noble and Garrett was repeated but no change found.

The values obtained for the solubility of the lead halides in water may be compared with those of other workers.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Temperature</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°C.</td>
<td>35°C.</td>
</tr>
<tr>
<td>PbCl₂</td>
<td>0.03858</td>
<td>0.04752</td>
</tr>
<tr>
<td></td>
<td>0.03893</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.03903</td>
<td>0.04767</td>
</tr>
<tr>
<td></td>
<td>0.03908</td>
<td>0.04742</td>
</tr>
<tr>
<td>PbBr₂</td>
<td>0.02621</td>
<td>0.03504</td>
</tr>
<tr>
<td></td>
<td>0.02655</td>
<td>0.03603</td>
</tr>
<tr>
<td></td>
<td>0.02674</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.02625</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.02638</td>
<td>0.03533</td>
</tr>
<tr>
<td>PbI₂</td>
<td>0.00165</td>
<td>0.00291</td>
</tr>
<tr>
<td></td>
<td>0.00165</td>
<td>0.00222</td>
</tr>
<tr>
<td></td>
<td>0.00166</td>
<td>0.00226</td>
</tr>
<tr>
<td></td>
<td>0.00164</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.00164</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.00163</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.00165</td>
<td>0.00224</td>
</tr>
</tbody>
</table>

According to the Born theory a plot of \( \log m \) against \( \frac{1}{D} \) should be linear. This is shown to be inapplicable to these results. Likewise the values of the Born radii are meaningless.
This is not surprising since the assumptions involved could not be expected to hold in these cases.

Calculations of activity coefficients using the Grönwall-La Mer extension are not possible in the absence of values of \( a \). The values of the activity coefficients, calculated from the Debye-Hückel equation using an arbitrary value of \( a \) and with neglect of incomplete dissociation, could not give thermodynamic functions of any value for comparison with theoretical values. For this reason they are not included in the results. Table IV serves only to indicate the type of values obtained.

Special Aspects of the Solubility of a Lead Halide in Mixed Solvents of Low Dielectric Constant

The dielectric constant range 2.10 to 79.55 obtainable from dioxane-water mixtures is an exceptionally wide one and therefore promises to be useful for studying the relations between solubility, dielectric constant, ionic diameters and degree of solvation of ions. This will become easier when satisfactory theories are brought forward to amplify Born's equation.

The neutral character, relatively high boiling point and complete miscibility with water are also very desirable properties of this solvent.

The major factors concerned in the solubility of these
salts in organic liquids are -
1. Ions may become associated. This is particularly important for a solvent of such a low dielectric constant as dioxane.
2. Ions may become solvated. The extent of the solvation may vary both in thickness and composition.
3. In the bulk solvent the unique structure of water may be broken down.

1. **Association of Ions** In solvents of low dielectric constant electrical forces between ions are sufficiently great to hold a large fraction of them in clusters. In the absence of accurate values for quantitative results are not possible. The method of Garrels and Guocker outlined in the introduction could possibly be used if approximate values of $K$ were known in the particular solvents.

2. **The Solvation of Ions** The nature of the solvent sheath about an ion will be a very important contributing factor.

   A. The effect of water in this shell. A small quantity of water in a solvent may cause a great increase in the solubility, a probable explanation being due to the formation of hydroxylic complexes. Pedesen found evidence for hydroxylic complexes of lead hydroxide and calculated their dissociation constants as functions of ionic strength, while Askew et alia when studying the heats of solution of electrolytes in non-aqueous solvents found specific effects which they considered
may indicate co-ordination between anions and hydroxylic hydrogen atoms. The fact that such a difficultly soluble substance as barium iodate should have detectable solubility in dioxanerich solvents as shown by Davis, Ricci and Sauter while its solubility in a single solvent of the same dielectric constant would probably be almost zero, is evidence that the preferential adsorption of water around ions has a large effect in determining solubility in solvents containing water.

In graph VI solubility curves for lead chloride in a number of mixed solvents are shown and give an interesting comparison of the relative solvation effects in mol for mol of solvent. It appears that the number and character of the polar groups in the solvent which is used with water is a factor determining the direction of the solubility effect. The dielectric constant of the mixture plays an important part, but a minor one compared with the "solvent character" effect.

B. Complex Formation. If the molecules of the first solvent sheath become sufficiently firmly bound to the central ion a complex solid phase is formed resulting in a sharp break in the solubility curve. It is generally assumed that, due to its rather complicated structure, the lead ion is responsible for the formation of the complex.

Complex formation is evident in dioxane for all three salts. A more complicated phase system seems to be present in the lead
Solubility of lead chloride in a number of mixed solvents at 25°C. Values according to Noble and Garrett, except for methanol (McGlashan)

\[ D = \text{Dielectric constant for the pure solvent at 25°C.} \]
iodide case. The bromide complex appears to be more stable than the chloride and iodide. Complexes of lead iodide and bromide with ethanol were found by Smith but as the temperature was increased the stability of the complexes decreased leading at higher temperatures to their disappearance. Complexes of all three halides with pyridine are known of the formula PbX₂ x(C₅H₅N) where x = 2 or 3 and similarly, those of the bromide are a little more stable than the chloride and iodide.

Various workers have reported the formation of dioxanates of inorganic halides especially those showing some degree of covalent character. Those of zinc and cadmium are shown below.

\[
\begin{align*}
\text{ZnCl}_2 \text{ (C}_4\text{H}_8\text{O}_2) & \quad \text{CdCl}_2 \frac{1}{2}\text{(C}_4\text{H}_8\text{O}_2) \\
\text{ZnBr}_2 \text{ 2(C}_4\text{H}_8\text{O}_2) & \quad \text{CdBr}_2 \text{ (C}_4\text{H}_8\text{O}_2) \\
\text{ZnI}_2 \text{ 2(C}_4\text{H}_8\text{O}_2) & \quad \text{CdI}_2 \text{ (C}_4\text{H}_8\text{O}_2)
\end{align*}
\]

Complexes of the elements arsenic, antimony and bismuth have been reported of the type 2AsCl₃ 3(C₄H₈O). All these dioxanates are white crystalline compounds separating immediately from anhydrous dioxane. The lead iodide dioxanates found during this work formed a white solid phase separating gradually from the yellow crystals of lead iodide.

C. The solvated ionic radius. This is defined as the distance from the centre of the ion to the electrical centre of gravity of the nearest solvent dipole and could not be expected to
correspond to the crystal radius. It is unreasonable to assume that this radius will remain constant in passing from water to pure dioxane. On the other hand, it is reasonable to suppose that ions in solutions containing small percentages of water will be fully hydrated or nearly so, so that for most of the dioxane water range a should be nearly constant.

Ricci and Nesse in a study of the solubilities of potassium and zinc iodates in dioxane water mixtures write, "The actual ion appears to be so intensively selectively solvated by the more polar solvent that it may be said that the concept of effective ionic radius here loses its meaning".

3. Breakdown in the Structure of Water In a mixed solvent the intrusion of the other solvent molecules will cause changes in the peculiar properties of aqueous solutions which have been connected with their open tetrahedral structure.

The Minimum Theory

In monohydrate alcohol water solvents various forms of the solubility curves can be correlated with the degree of covalency of the salt.

(1) Strong electrolytes decrease steadily in solubility passing from water to alcohol.

(2) Highly covalent compounds such as CdI₂ and HgI₂ increase steadily in solubility from water to alcohol.

(3) Intermediate compounds.
(a) Relatively salt-like compounds like PbI$_2$ decrease at first but as the alcohol concentration rises the rate falls off and passes through a minimum near pure alcohol.

(b) Relatively covalent compounds like HgCl$_2$ in ethanol decrease in solubility only slightly passing through a minimum in solutions of low alcohol content and then rising to a higher solubility in pure alcohol than in pure water.

On this basis the minimum in the lead iodide curves can be interpreted as representing the composition of the solvent at which the tendency of lead iodide to behave as a salt is balanced by its weaker tendency to dissolve as a covalent compound. A theoretical interpretation was given to this by Smith who considered that a major factor would be ionic association on a similar mechanism to that suggested by Fuoss and Kraus. For lead iodide the increasing size of the lead ion with increasing alcohol in the solvent must be such that its "breaking down" upon the water structure added to the parallel effect of increasing alcohol concentration reaches such a magnitude at a certain composition of solvent that the water is no longer able to function as an ionizing solvent. From that point, the observed minimum, on to pure alcohol lead iodide dissolves in the manner of a covalent compound in a non-ionizing solvent. Smith further suggested it possible that all salts actually exhibit minima in their solubility curves but since they would be so near pure alcohol or pure water they would be very difficult to detect experimentally. The position of a
minimum in a solubility curve would thus be a measure of the covalency of the bonding in any solute.

One of the original purposes of the present work was to test this theory since the presence of a definite minimum for lead iodide in dioxane would show that the effect of ionic association was the predominant one depending as it does on the effect of decreasing dielectric constant. Unfortunately complex formation has been superimposed on the results but it is perhaps significant that there is a decrease in the slopes of the solubility curves (see Graph VII) in the order of increasing covalency of the salts, that is chloride, bromide and iodide and that had complex formation not occurred a slight minimum might have been observed for lead bromide and a greater one for lead iodide.

The Results of Other Workers using Solvents of Low Dielectric Constant

Vernon, Luder and Giella\textsuperscript{50} when studying the solubility of the strong electrolyte tetrabutylammonium iodide in benzene (\(D = 2.28\)) in the presence of other tetrabutylammonium salts found a rapid increase in solubility. If single ions were involved the solubility of the iodide would decrease rather than increase with the addition of a common ion so that these results would confirm the conclusion that solutions of salts in solvents of very low dielectric constant are associated.
GRAPH VII

Solubility of Lead Halides at 25°C.
The behaviour of hydrochloric acid in dioxane water mixtures has been investigated and activity coefficients determined from cell data. The contribution of the extended terms of the Debye-Hückel equation are so small in the case of 4.67 mols % dioxane that they do not alter the ordinary extrapolation but between this and 50 mols % they explain the results well. After this the extended equation ceases to be satisfactory and another method involving dissociation constants derived from conductance measurements was used. This means that the hydrochloric acid is showing in these solvents the characteristic behaviour of a weak electrolyte.

Fuoss and Kraus have determined the equivalent conductance of tetraisoamylammonium nitrate in dioxane water mixtures. When the dielectric constant of the solvent is of the order ten or less a minimum is observed in the conductance curves (concentration against conductance) and with further decrease of dielectric constant the minimum becomes more distinct and shifts in the direction of increasing dilution. This increase in the number of ions could be due to combination of ions with ion pairs to form "triple ions" or even "quadruples".

The Ricci Davis postulate of constant activity coefficient and the Born equation for potassium and zinc iodates in dioxane water mixtures was tested by Ricci and Nesse and found satisfactory as to the order of magnitude up to about 17 mols % dioxane. By taking a value of 2.5A° for a, theoretical
solubilities were calculated from the Debye-Hückel and Born equations but except for very low dioxane solvents the agreement was not good, the calculated values being far less than the observed. An attempt was made to modify the Born equation for segregation of solvent molecules by ions in mixed solvents but this over accounted for the large negative error.

The solubility of silver sulphate, silver acetate and barium iodate in dioxane water mixtures was determined by Davis, Ricci and Sauter\textsuperscript{48}. The solubility was also determined in the presence of other electrolytes in the 2.2 and 4.6 mols \% dioxane whereby activity coefficients were determined and a values calculated from the Debye-Hückel equation. At very low ionic strengths for these solvents, the limiting slopes of the curves $-\log \gamma_2$ against $\sqrt[12]{c}$ are in fair agreement with the limiting law.

The solubility curves of these five salts up to 65\% dioxane are shown in graph VIII. where those of this work are also included for comparison. In graphs IX and X log m is plotted against $\frac{1}{D}$ and log D respectively. The graphs illustrate the approximate linearity of some of these salts in the low percentage dioxane mixtures. In this respect the lead halides show greater variance.

Finally the values of $\gamma_2$ determined by Noble and Garrett\textsuperscript{37} for lead chloride in 4.67, 12.0 and 23.5\% dioxane, by determining the solubilities in the presence of potassium nitrate, are plotted against $\sqrt[12]{c}$ in graph XI. The limiting slopes are
indicated. These are 1.69, 2.73 and 8.00 respectively, all of which are larger than the theoretical slopes calculated from the limiting law.

The results of these workers serve to confirm that extensive theoretical elucidation is necessary before activity coefficients can be calculated in high concentration dioxane solutions.
Solubility of Various Salts in Dioxane-water Mixtures up to 65% Dioxane at 25°C.
GRAPH IX

\[ \log m \]

\[ (D) \rightarrow \]

- \( Ag_2Ac \)
- \( KIO_3 \)
- \( Zn(IO_3)_2 \)
- \( Ba(IO_3)_2 \)

\( Ag_2SO_4 \)
Lead Chloride in Dioxane-water Mixtures at 25°C. Values according to Noble and Garrett.
SUMMARY

1. The solubility of lead chloride, bromide and iodide in dioxane-water mixtures has been determined at 25°C., 35°C. and 45°C.

2. Born radii have been calculated for these salts at 25°C.

3. Activity coefficients at 25°C. have been calculated using the Debye-Hückel equation and values of the thermodynamic solubility products and free energies have thereby been calculated.

4. Special aspects of solubility in mixed solvents, including the minimum theory, have been discussed accounting for the failure of theoretical equations outlined in the introduction to be applied to the results.

5. Some of the results of other workers, using solvents of low dielectric constant, are discussed.
1. Gronwall, La Mer and Sandved
2. Gronwall, La Mer and Grieff
3. Bjerrum
4. Fuoss and Kraus
5. Hogge and Garrett
6. M.C. Hannan
7. Fromherz
8. Righellato and Davies
9. Garrels and Gucker
10. Scatchard and Teft
11. Harned and Fitzgerald
12. Born
13. Latimer, Pitzer and Slansky
14. Dunning and Shutt
15. Bell and Gatti
16. Ricci and Davis
20. Baxter and Grover
21. Baxter and Thorvaldson
22. Eigenberger
23. Weissberger and Proskauer
24. Kolthoff, Lauer and Sunde
25. Hamann
26. Smith
27. Scott

Physik. Z. 29, 558 (1928)
J. Chem. Phys. 35, 2245 (1931)
Kgl. Danske Vidensk. Selskab, 7, No. 9 (1926)
J.A.C.S. 55, 2387 (1933)
J.A.C.S. 52, 1089 (1941)
See reference 9.
Z. Physik. Chem. 153, 382 (1931)
T.F.S. 26, 592 (1930)
Chem. Rev. 44, 117 (1949)
J.A.C.S. 52, 2272 (1930)
J.A.C.S. 52, 2624 (1936)
Z. Physik. 1, 4 (1920)
T.F.S. 34, 1192 (1938)
Phil. Mag. 19, 66 (1935)
J.A.C.S. 62, 407 (1940)
J.A.C.S. 37, 1051 (1915)
J.A.C.S. 37, 1020 (1915)
E., J.pr. Chem. 130, 75 (1931)
"Organic Solvents" p.38
J.A.C.S. 51, 3273 (1929)
Thesis, Univ. of N.Z. (1946)
Thesis, Univ. of N.Z. (1947)
Standard Methods of Chemical Analysis 5th ed. p.521
28. Craig and Vinal
29. Cox
30. MacInnes and Dole
31. Hall, Jensen and Baeckstrom
32. Jones and Hartmann
33. Lange and Schwartz
34. Snell and Snell
35. Akerlof and Short
36. Hovorka et Alia
37. Noble and Garrett
38. McGlashan
39. Lichty
40. Randall and Vietti
41. Herz and Hellebrandt
42. Wood
43. Burrage
44. Lanford and Kiehl
45. Van Klooster and Balon
46. Pedesen
47. Askew
48. Davis, Ricci and Sauter
49. Ricci and Hesse
50. Vernon, Luder and Giella
51. Fuoss and Kraus

J. Research National Bureau of Standards 22, 55 (1939)

J.A.C.S. 47, 2138 (1925)
J.A.C.S. 51, 1119 (1929)
J.A.C.S. 50, 2217 (1928)
J.A.C.S. 37, 756 (1915)
Z. Ph. Ch. 129, 111 (1927)

Colourimetric methods of Analysis Vol. 1, p.204

J.A.C.S. 58, 1241, (1936)
J.A.C.S. 58, 2264 (1936)
J.A.C.S. 66, 231 (1944)
Theis, Univ. of N.Z. (1945)

J.A.C.S. 25, 469 (1903)
J.A.C.S. 50, 1526 (1923)
Z. anorg. all. Ch. 130 188 (1923)
Theis, Univ. of N.Z. (1943)

J.C.S. 129, 1703 (1926)
J.A.C.S. 63, 667 (1941)
J.A.C.S. 56, 591 (1934)
Kgl. Dansk. 22, 9 (1945)
J.C.S. 137, 1368 (1934)

J.A.C.S. 61, 3274 (1939)
J.A.C.S. 64, 2305 (1942)
J.A.C.S. 63, 862 (1941)
J.A.C.S. 55, 1019 (1933)