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ELECTROCHEMICAL INVESTIGATION OF THE TRANSITION FROM TETRAGONAL TO CUBIC CÆSIUM PLUMBO CHLORIDE

BY

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Synopsis

The cæsium halide concentrations for which Cs_4PbX_6 and $CsPbX_3$ (X = Cl or Br) together may be in equilibrium with aqueous solutions of CsX have been determined as a function of the temperature, and the range of stability for $CsPbX_3$ alone in equilibrium with such solutions at room temperature has also been obtained. Measurements at a series of temperatures of the e.m.f. of electrochemical cells, where crystalline $CsPbCl_3$ is involved in the electrode processes allow a determination of the entropy change, ΔS, for the process $CsPbCl_3$(tetragonal) → $CsPbCl_3$(cubic). The value thus obtained is $\Delta S = 4.0$ cal/mol. degree. On the assumption that the process is essentially an order-disorder tranformation, an elementary calculation based on Boltzmann's relation gives $\Delta S = 4.1$ cal/mol. degree. The results are compared with those for $BaTiO_3$.

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Introduction

Perovskite-like crystals usually undergo a transition from slightly distorted cubic to true cubic structure at one temperature or another. Sometimes there is a simultaneous, great change in dielectric properties, e.g. in $BaTiO_3$ from a ferroelectric to a paraelectric state.[1] It has been suggested that these might be cases of "second order transitions", and the temperatures at which they occur are often named λ-points or Curie-points.

The term second-order transition was first used by EHRENFEST[2] to describe a type of transition for which the G-function and the entropy $S = -\left(\frac{\partial G}{\partial T}\right)_p$ are continuous, while $C_p = T\left(\frac{\partial S}{\partial T}\right)_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p$ shows a discontinuity. According to FRENKEL,[3] however, as true examples of such transitions have never been observed and are not likely to correspond to a stable equilibrium between two phases, it seems preferable to characterize a second-order transition in crystals with the following features:

A certain (super-)order of the atomic arrangement decreases *continuously*, though at an ever increasing rate until it vanishes completely at a certain temperature, T_0. The specific heat at constant pressure, C_p, shows an abnormal rise, reaching a finite or infinite peak value at T_0 and *rapidly dropping to its normal value as the temperature is raised beyond the point* T_0.

Hence, from a purely thermodynamic point of view transitions of the second order may be treated as a generalization of transitions of the first kind with the transition temperature T' replaced by a certain temperature range ΔT about T'. The latent heat for the change is replaced accordingly by the integral $\int \Delta C_p dT$, where ΔC_p denotes the excess of the specific heat over its normal value. Also a first-order transition may be described as a limiting case of that of the second order with a specific heat anomaly ΔC_p represented by a delta-function.

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[1] See e.g. H.D. MEGAW, *Ferroelectricity in Crystals*, Chapters 4 and 5. Methuen 1957.

[2] See e.g. E.A. GUGGENHEIM, *Thermodynamics*, p. 276—288. North-Holland Publishing Co. 1949.

[3] J. FRENKEL, *Kinetic Theory of Liquids*, Chapter II. Oxford 1946.

Throughout this paper we have adopted FRENKEL's point of view. It will then be understood that the two types of transitions should not be contrasted with one another, but only considered ideal extremes of actual thermodynamic transitions.

If we have a series of discrete first-order transitions taking place within a narrow temperature range and each separately represents only a small change of the entropy, it seems legitimate, from a purely thermodynamic point of view, to treat the total change as a second-order transition. It would appear futile to discuss whether the transition properly belonged to the one type *or* the other—the more so as there will often be unavoidable hysteresis phenomena.

The perovskite-like crystals of $CsPbCl_3$ and $CsPbBr_3$ undergo transitions from a tetragonal super-lattice to a primitive cubic lattice at 47 °C. and 130 °C., respectively, which fulfil some of the requirements for second-order transitions.[1] In the work referred to, no volume change was observed at the transitions, but a small anomaly (discontinuity) was found in the thermal expansion coefficient $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ for $CsPbCl_3$. As there is a certain parallellism between changes of the latter and changes of the heat capacity at constant pressure,[2] ΔC_p, this would indicate an anomaly in C_p also. It was suggested that the observed transitions were connected with order-disorder transformations rather than drastic changes in the kinematic state of certain ions.

To reach a better understanding of the nature of these transitions it was chosen to study more closely the simultaneous changes in the thermodynamic functions, G (thermodynamic potential) and S (entropy) of $CsPbCl_3$. As the transition temperature here is only 47 °C. this can be done by ordinary wet chemical methods, e.g. by measuring the electric potential of electrochemical cells whose electromotive force depends on the chemical potential of crystalline $CsPbCl_3$ in equilibrium with an aqueous solution of CsCl. Before this could be done it was necessary to determine the range of stability of such systems.

In the following X means either Cl or Br.

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[1] C.K. MØLLER, *The Structure of Perovskite-like Cæsium Plumbo Trihalides*, Mat. Fys. Medd. Dan. Vid. Selsk. **32** No. 2 (1959).

[2] See J. FRENKEL, *loc. cit.* p. 76.

The Equilibrium of $CsPbX_3$ with Aqueous Solutions of CsX

When the concentration of CsX in aqueous solution changes from that of saturated to that of very dilute solutions the composition of the stable Pb-compounds in equilibrium with it changes from Cs_4PbX_6 through $CsPbX_3$ and $CsPb_2X_5$ to PbX_2. It follows from the phase rule that at a given temperature one definite Pb-compound will be in equilibrium with CsX-solutions over a certain range of CsX-concentrations; for two different Pb-compounds to be in equilibrium with the same CsX-solution at a definite temperature only one CsX-concentration exists. This will then be the concentration at which the composition of the precipitate changes at that temperature.

On this basis we have determined the equilibrium temperatures for the process $Cs_4PbX_6 \rightleftarrows CsPbX_3 + 3\,CsX(aq.)$ as a function of aqueous CsX-concentrations. A series of CsX-solutions of known concentrations were made. A few crystals of $CsPbX_3$ and Cs_4PbX_6 were placed side by side in a hollow microscope slide and a drop of one of the CsX-solutions added. A cover glass was quickly put over it, "sealed" to the microscope slide with paraffin oil to make a closed space from which no water could evaporate. The slide with its contents was placed upside down, i.e. with the liquid drop hanging down from its concave side, on a hot stage. By this procedure water condensation on the cover glass was avoided during heating of the specimen.

The crystals in the drop of CsX-solution were carefully watched through a microscope. If nothing happened, the specimen was slowly heated till changes of the crystals could be observed. This was much easier to see than one would think, and as a matter of fact even a first trial usually gave the transition temperature within 5°C. After heating to above this temperature, the changes occurring during cooling were observed and the temperature interval for the transition narrowed by subsequent experiments. As an example fig. 1 shows how the crystals in equilibrium with a certain CsCl-solution changed when the temperature was varied.

An alternative method was also used for the Br-compounds. It is based on the fact that $CsPbBr_3$ is strongly orange-coloured while Cs_4PbBr_6 is colourless. In a very small test tube attached to a thermometer a sample of Cs_4PbBr_6-crystals was placed, about 0.7 cc. of a CsBr-solution of known concentration was added, and the test tube well corked. The thermometer and the test tube with its contents were very slowly heated in a small water bath and the temperature at which the colour of the crystals suddenly turned orange was noted.

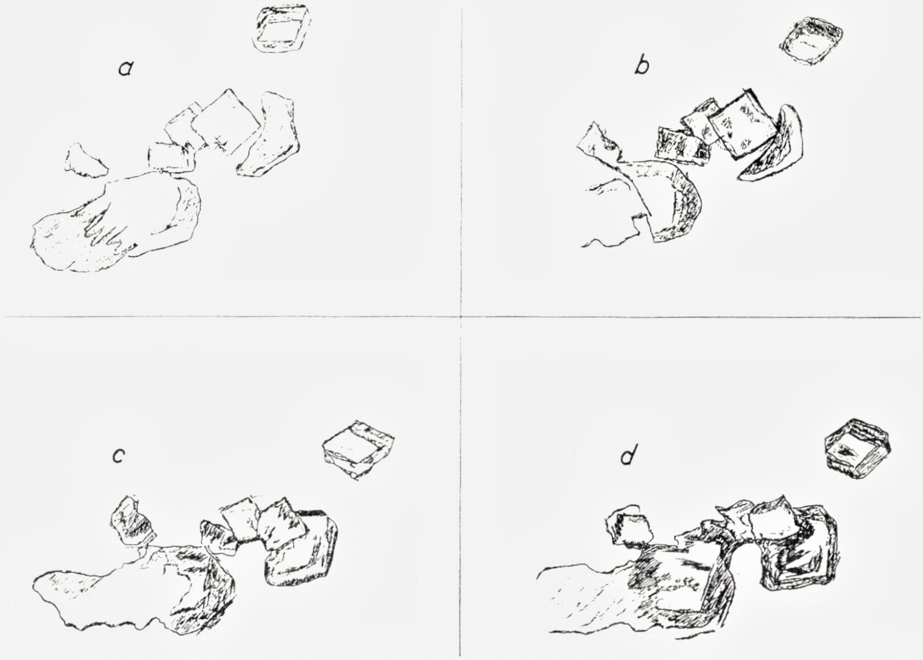

Fig. 1. Crystals of Cs_4PbCl_6(rhombohedral) and $CsPbCl_3$(cubic) in equilibrium with a CsCl-solution at different temperatures (drawn by means of an Abbe's drawing apparatus; magnification 100 ×).

a:	Time:	0 ;	temp.	22° C.
b:	–	10 m;	–	22° C.
c:	–	85 m;	–	19° C.
d:	–	110 m;	–	18° C.

There was good agreement between the two methods, but the latter is by far the quickest where it can be applied. It is believed that the equilibrium temperatures (as a function of the CsX-concentrations) have been determined with an accuracy of ± 2° C. An obvious advantage of these methods is the small amount of material that is necessary, and for several purposes, e.g. when, as here, only an estimate of the stability range is required they may be of sufficient accuracy.

The cæsium halogenides used for the experiments were the very pure salts prepared by Lannung or prepared from his very pure Cs-alums by the method described by him.[1] PbX_2-compounds were precipitated from aqueous solutions of $Pb(NO_3)_2$ (Merck, "rein") and very pure HX, and recrystallized several times from hot, dilute solutions of HX (pH ≈ 1).

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[1] A. Lannung, *Z. phys. Chem.* Abt. A. **161**, 255 (1932).

The compounds $CsPbX_3$ and Cs_4PbX_6 were precipitated from aqueous solutions of these materials as previously described.[1]

The compositions of the CsX-solutions were determined by evaporating to dryness (final temperature 120° C.) weighed samples of the solutions and then weighing the residues again.

As attainment of the equilibrium $2CsPbX_3 \rightleftarrows CsPb_2X_5 + CsX(aq.)$ was very sluggish, the CsX-concentrations for it to occur were determined only at room temperature and by the first of the two methods mentioned above.

Stability Range of $CsPbX_3$

The results of the experiments mentioned above are reproduced in Table 1 and in figs. 2 and 3.

TABLE 1. Equilibrium concentrations and temperatures

System	Aqueous CsX-conc.		Equilibrium temp. t_e °C.	Estimates of ΔH cal/mol.
	g CsX per 100 g H_2O	x_e, mole fraction of X^- or Cs^+		
$Cs_4PbCl_6 \rightleftarrows CsPbCl_3 + 3CsCl$	151	12.2_0 10^{-2}	63—64	6100
	144.5	11.8_0 –	58	
	141	11.5_8 –	49—50	
	135	11.2_0 –	45—46	
	122	10.3_4 –	31—32	
	113	9.7_3 –	20	
$2CsPbCl_3 \rightleftarrows CsPb_2Cl_5 + CsCl$	20	2.0_5 –	$t_e \approx 58°$	
	15	1.5_5 –	20	
$Cs_4PbBr_6 \rightleftarrows CsPbBr_3 + 3CsBr$	109	7.7_8 –	69.5	16400
	87	6.4_1 –	51	
	75	5.6_3 –	43	
	67	5.0_9 –	37	
	55	4.2_5 –	24.5	
$2CsPbBr_3 \rightleftarrows CsPb_2Br_5 + CsBr$	23.5	1.9_1 –	$t_e > 20°$	
	20.5	1.6_8 –	20	
	18.8	1.5_4 –	$(t_e < 20°)$	

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[1] C.K. MØLLER, *Mat. Fys. Medd. Dan. Vid. Selsk.* **32** Nos. 1, 2, and 3 (1959) and (1960).

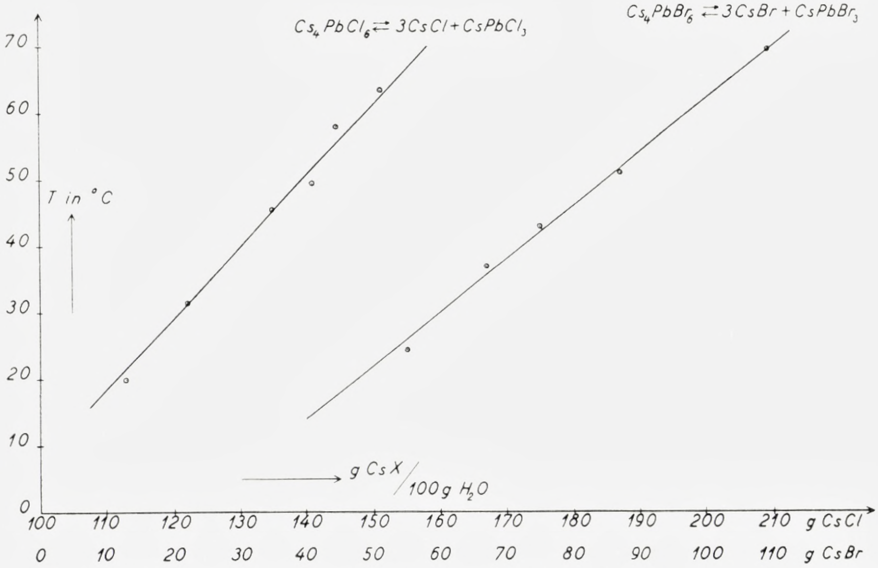

Fig. 2. The equilibrium temperature for $Cs_4PbX_6 \rightleftarrows CsPbX_3 + 3Cs^+ + 3X^-$ as a function of the aqueous CsX-concentration.—The lower horizontal scale refers to CsBr, the upper one to CsCl.

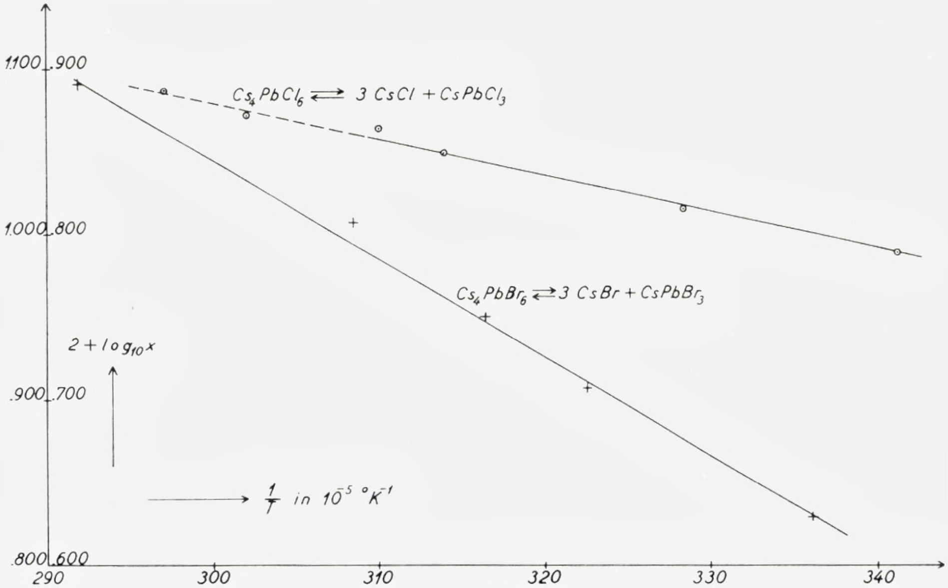

Fig. 3. $\text{Log}_{10}\, x_c$ as a function of the inverse equilibrium temperature in °K. The left ordinate scale refers to CsCl, the right to CsBr.

Within the experimental uncertainty it appears that the CsX-concentrations for which the equilibrium

$$Cs_4PbX_6 \rightleftarrows CsPbX_3 + 3\,Cs^+ + 3\,X^- \tag{1}$$

can be established, depend linearly on the temperature. If we neglect the temperature dependence of the chemical potentials of the crystalline solids and of the activity coefficients for CsX in solution we can estimate the heat of reactions for the above processes from VAN'T HOFF's relation expressed as follows:

$$(\log_e K =)\ 3\,\log_e x_e^2 = 13.815\,\log_{10} x_e = -\frac{\varDelta H}{RT} + \text{const.}, \tag{2}$$

where x_e is the ionic mole fraction of Cs^+ or Cl^- at the equilibrium (1), These estimates, which should not be considered very accurate, are given in the last column of Table 1.

In principle it should be possible to determine the entropy change for the reaction

$$\text{Tetragonal } CsPbCl_3 \rightleftarrows \text{Cubic } CsPbCl_3 \tag{3}$$

from measurements of $\varDelta H$ for (1) above as well as below the transition temperature (47° C.) for (3). Unfortunately it becomes increasingly difficult to obtain reliable values for the CsCl-concentrations as functions of the temperature above 55° C. because the solubility of the $CsPbCl_3$ becomes too great so that the actual CsCl-concentration is not accurately known; nor was in our case the temperature in the hollow microscope slide sufficiently well determined at higher temperatures. And finally it would be necessary to use CsCl-activities instead of concentrations in order to derive rather small entropy changes.

The sluggishness of the reaction

$$2\,CsPbX_3 \rightleftarrows CsPb_2X_5 + CsX(\text{aq.}) \tag{4}$$

is presumably connected with the rather drastic changes of the PbX-coordination taking place here: In $CsPbX_3$ and Cs_4PbX_6, Pb is approximately octahedrally coordinated by the halogen ions, whereas the $CsPb_2X_5$-compounds are likely to contain PbX_2-"molecules".[1]

It is interesting that H.L. WELLS has described a dimorphous form of $CsPbBr_3$, said to be stable in a narrow CsBr-concentration interval close to the equilibrium for (4) with X = Br.[2]

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[1] Cf. H.M. POWELL and H.S. TASKER, *J. Chem. Soc.* London, 1937, p. 119 and Ref. 1 on page 7.

[2] H. L. WELLS, *Z. anorg. Chem.* **3**, 203, (1893).

In this region we also have seen crystals which closely correspond to the characteristics given by WELLS: They were white, needle-shaped, showed parallel extinction, and on heating to 140–150 °C. they turned orange-coloured. But it looks as if also $CsPbCl_3$ is dimorphous: Occasionally white needle-shaped crystals having parallel extinction can be seen in the CsCl-solutions when the concentration is only slightly higher than that corresponding to the equilibrium (4) with X = Cl. Although no *X*-ray diagrams have so far been obtained of the white needle-shaped crystals, it seems very tempting to guess that they are the Cl- and Br-analogues to the orthorhombic $CsPbI_3$-crystals[1] and thus represent one of the stages in changing the Pb-coordination.

Principle of the Electrochemical Determination of the Entropy Change

Let us consider an electrochemical cell of the type

$$\mathrm{Pt} \mid \mathrm{Pb(Hg)} \mid \mathrm{PbCl_2} \mid \text{Aqueous solution of NaCl} \mid \mathrm{Hg_2Cl_2} \mid \mathrm{Hg} \mid \mathrm{Pt}, \quad (5)$$

where Pb(Hg) denotes a Pb-amalgam saturated with Pb. The chemical process when two faradays flow from the left to the right is:

$$\mathrm{Pb(Hg)} + \mathrm{Hg_2Cl_2} \rightarrow 2\,\mathrm{Hg} + \mathrm{PbCl_2} \quad (6)$$

Similarly, when the CsCl-concentration is kept within the limits for which $CsPbCl_3$ is stable, the chemical process accompanied by the flow of two faradays through the cell

$$\mathrm{Pt} \mid \mathrm{Pb(Hg)} \mid \mathrm{CsPbCl_3} \mid \text{Aqueous solution of CsCl} \mid \mathrm{Hg_2Cl_2} \mid \mathrm{Hg} \mid \mathrm{Pt} \quad (7)$$

is:

$$\mathrm{Pb(Hg)} + \mathrm{Hg_2Cl_2} + \mathrm{CsCl\,(aq.)} \rightarrow 2\,\mathrm{Hg} + \mathrm{CsPbCl_3}\,. \quad (8)$$

Hence the difference in electromotive forces of the two cells, $\pi_6 - \pi_8$, is a measure of ΔG for the process

$$\mathrm{PbCl_2} + \mathrm{CsCl\,(aq.)} \rightarrow \mathrm{CsPbCl_3} \quad (9)$$

and

$$\pi = \pi_6 - \pi_8 = \frac{1}{2F}\left\{\mu(\mathrm{CsPbCl_3}) - \mu(\mathrm{CsCl,aq.}) - \mu(\mathrm{PbCl_2})\right\}, \quad (10)$$

or

$$\mu(\mathrm{CsPbCl_3}) = 2F\pi + RT\log_e\left\{\mathrm{a}(\mathrm{CsCl,aq.})\right\} + \mu(\mathrm{PbCl_2}) + \mu_0(\mathrm{CsCl,aq.}), \quad (11)$$

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[1] Cf. Ref. 1 on page 7.

where $\mu_0(\mathrm{CsCl,aq.})$ is independent of the CsCl-concentration. Hence it is not possible in this way to obtain absolute values of the chemical potential for $CsPbCl_3$ unless we know the activity of CsCl in aqueous solution and the chemical potential for $PbCl_2$. However, we shall not be particularly interested in absolute values of the potentials, but only in the changes of the chemical potential of $CsPbCl_3$ as a function of temperature. It seems safe to assume that $\mu(\mathrm{PbCl_2})$ and $\mu(\mathrm{CsCl,aq.})$ vary only slowly with temperature so that any sharp or rapid variation of π or, as experiments show that π_6 is a linear function of temperature within the temperature interval for the investigation, of π_8 is produced by similar changes in the chemical potential of $CsPbCl_3$.

The changes in G-function and in entropy of $CsPbCl_3$(cryst.) at 47°C. may therefore be obtained from the temperature variation of π_8 measured above as well as below 47°C.:

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_p \backsim 2F\left\{\left(\frac{\partial \pi_8}{\partial T}\right)_{>47^\circ} - \left(\frac{\partial \pi_8}{\partial T}\right)_{<47^\circ}\right\}. \tag{12}$$

If the CsCl-concentration in (8) is kept so high that a Cs_4PbCl_6-electrode may be used instead of the $CsPbCl_3$-electrode the reaction expressed in (1) can be examined in the same way. Furthermore, as Cs_4PbCl_6 is stable in a solution saturated with CsCl, the activity of CsCl in aqueous solution with concentration m can be related to the chemical potential of CsCl in crystalline CsCl from measurement of the electric potential difference of such cells of which one contains a saturated CsCl-solution, the other a CsCl-solution of concentration m as electrolyte. Unfortunately the Hg_2Cl_2-electrode turned out not to be reliable at such high CsCl-concentrations.

The diffusion potential in the cells mentioned above have been neglected because the CsCl-concentration in every case is much higher than the concentrations of Pb^{++} and Hg_2^{++} around the electrodes, so that they are practically "cells without transference".

Experimental Details

Rather small electrode vessels requiring about 1 cc. of electrolyte were used. They were H-shaped with Pt-electrodes sealed into the bottom. A loose plug of cotton wool was placed between the two electrodes. The branch with Pb-amalgam also contained a small (glass-covered) magnetic stirrer as stirring here sometimes was necessary in order to obtain reproducible measurements. The temperature of the cells was controlled within 0.02° C. by an oil thermostat.

The quality of the chemicals were as follows: Hg, cleaned in dilute nitric acid and distilled in vacuum; Pb-amalgam (always containing solid phase) made from distilled Hg and Merck's Pb pro analysi. Other Pb-compounds were prepared as mentioned above. Except for preliminary experiments, where rather impure CsCl was used, "AnalaR" or Lannung's spectroscopically pure CsCl was used (both giving the same results within the accuracy of the measurements).

The electrolyte solutions were made by adding a definite amount of water to a weighed sample of CsCl and the composition was checked after the often very long experiments by taking out a certain amount of the electrode solution, weighing it, and after evaporation of the liquid, weighing the residue again.

This final determination is considered to indicate the CsCl-concentration in the cells during the measurements, as it is difficult to avoid some evaporation while preparing the cells.

Measurements of the electromotive forces were made by the usual compensation method, using a precision potentiometer, a 2 volt lead accumulator, galvanometer, and a standard Cd-cell ($E = 1.0184$ volt at 20° C., checked occasionally by comparison with an International standard cell). The uncertainty presumably is not higher than 0.1 mV.

The cells with Cs_4PbCl_6, which required rather concentrated CsCl-solutions, did not give steady potentials (except when saturated with CsCl), and when the CsCl-content of the electrolyte solution was examined after the experiments it had often changed by 5–10 per cent. It was observed in such cases that the Hg_2Cl_2-electrode became grey or dark grey and had developed a hard, solid crust, suggesting the formation of double compounds according to the reactions:

$$\left.\begin{array}{r} Hg_2Cl_2 \rightarrow Hg + HgCl_2 \\ n\,CsCl + HgCl_2 \rightarrow Cs_nHgCl_{n+2}\,. \end{array}\right\} \quad (13)$$

However, the cells with $CsPbCl_3$ and less concentrated CsCl-solutions seemed very reliable when stirred now and then. While equilibrium was very quickly re-established in the cells when going from one temperature to a higher one, they often showed 0.3–0.5 mV. higher potentials at 20° C. after cooling from 60° C. than when measured before heating to this temperature. This change may possibly be due to slow or irreversible diffusion processes, either in the electrolyte solution or in the $CsPbCl_3$-crystals. It might perhaps also be due to evaporation even though the cells were well corked and immersed in oil; however, they showed no significant variation in potential when kept for several days at 60 °C. (A change of 0.5 mV. would correspond to a little less than a two per cent change of the CsCl-concentration).

Table 2 shows examples of the daily variation of the potentials of some of the cells.

The averages of several measurements at each of a series of selected temperatures are given in Tables 3 and 4 for a number of cells of Type (7), some cells of Type (5), and one having $CsPb_2Cl_5$ instead of $CsPbCl_3$.

Results

The variation of the measured potentials with the logarithm of the ionic mole fraction, x, of Cs^+ or Cl^- in the cells (7) is shown in fig. 4 for different temperatures. It is seen that for a given temperature, and for the CsCl-concentrations considered, the potential π_8 is a nearly linear function of $\log_{10} x$ of the form

$$\pi_8 = \beta \log_{10} x + b\,. \tag{14}$$

The relation to be expected is from (8) and (10):

$$\pi_8 = 2.3026 \cdot \frac{RT}{F} \log_{10}(x f_\pm) + a = \alpha \log_{10}(x f_\pm) + a\,. \tag{15}$$

From Robinson and Stokes's tables of activity coefficients[1] it appears that $f_\pm$ should be practically independent of x for the CsCl-concentrations used here. Hence, if the process in the cells really is the one expressed in (8) β would be expected to be identical with the theoretical value α—or nearly so. The smallness of the relative deviations:

$$\eta = \frac{\beta - \alpha}{\alpha} \tag{16}$$

shown in the graph fig. 5 in fact warrants the correctness of the assumption.

Before discussing the reason why β and α are not identical it should be emphasized that the CsCl-concentrations in the cells have not been determined with any high accuracy—the relative uncertainty may indeed be as high as 2–3 per cent. (The original aim was only roughly to check the cell process, and hence no correction was made for the possible Pb-contents

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[1] R.A. Robinson and R.H. Stokes, *Trans. Far. Soc.* **45**, 613 (1949).

TABLE 2. Examples of the daily variation in electromotive force of the cells.

Date	Temp. °C.	E.m.f. in mV. of the cells		
		P	*R*	*S*
30.11 a. m.	20.00	577.0_4	562.3_0	529.2_8
— — — —	—	577.0_2	562.3_0	529.2_5
— — p. m.	30.00	576.1_8	560.4_5	530.1_3
— — — —	—	576.1_5	560.4_5	530.4_0
1.12 a. m.	—	576.1_6	560.5_6	530.3_5
— — — —	—	576.1_2	560.5_2	530.3_6
		stirred	stirred	stirred
— — p. m.	—	576.1_3	560.4_8	530.1_8
— — — —	—	576.1_8	560.5_5	530.1_8
2.12 a. m.	—	576.1_5	560.5_7	530.2_7
17.12 a. m.	50.50	575.3_0	558.3_5	533.3_1
— — — —	—	575.2_8	558.3_4	533.3_0
— — p. m.	55.00	575.1_5	557.9_5	533.8_0
— — — —	—	575.1_8	557.9_3	533.8_5
18.12 a. m.	—	575.1_5	557.9_6	533.8_5
— — — —	—	575.1_5	557.9_8	533.8_8
		stirred	stirred	stirred
— — p. m.	—	575.1_9	558.0_0	533.9_0
— — — —	—	575.2_3	558.0_2	533.9_0

of the samples taken out from the cells). E. GÜNTELBERG[1] has shown that even with very pure materials small amounts of Br^- or other unwanted ions in the cell solutions may be troublesome when very accurate e.m.f.-measurements have to be made. This effect has also been disregarded here.

The observed differences between β and α would imply that the mean activity coefficient $f_\pm$ for the CsCl-concentrations considered was approximately given by:

$$\log_{10} f_\pm = \eta \log_{10} x + \sigma\,, \tag{17}$$

where σ may depend on the temperature, but not on x. This is not quite in accordance with the results given by ROBINSON and STOKES, but the the electrometric measurements by HARNED and SCHUPP[2] are in fact compatible with (17), and the value obtained for η for this concentration interval is nearly the same as found here at 25° C., when regard is paid to the rather large uncertainty on η: ± 0.01.

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[1] E. GÜNTELBERG, *Studier over Elektrolyt-Aktiviteter i vandige Opløsninger.* Dissertation, Copenhagen 1938.

[2] H.S. HARNED and O.E. SCHUPP, J. Am. Chem. Soc. **52**, 3886. (1930).

If we neglect the temperature variation of σ in (17) an estimate of the partial molar heat of transfer, Q, from an infinitely dilute solution of CsCl in H_2O to the CsCl-concentrations considered may be obtained from

$$\frac{\partial \log_{10} f_{\pm}}{\partial \left(\frac{1}{T}\right)} = 2.303 \cdot \log_{10}(x) \cdot \frac{\partial \eta}{\partial \left(\frac{1}{T}\right)} = \frac{Q}{R}\,. \tag{18}$$

We find $Q \backsimeq -R\,2.303 \cdot 135 \cdot \log_{10}(x)$ which for a 2 molal CsCl-solution becomes $Q \backsimeq 900$ cal/mol.

The potentials π_8 for given CsCl-concentrations are shown as functions of the temperature in fig. 6; for comparison the results of measurements

Tables 3, 4, and 5. Electromotive forces of cells with different electrolyte concentrations at a series of temperatures from 18°C. to 60°C.

Table 3.

Cell	*K*	*L*	*M*
g CsCl/100 g H_2O	41.5	64.0	52.2
Temp. °C.	E.m.f. in mV.		
18.02	576.1_2	585.7_4	581.5_2
25.00	575.4_8	585.4_9	—
32.05	574.9_2	585.2_8	—
39.00	574.4_7	585.1_4	—
40.00	574.4_0	585.1_3	580.3_6
41.00	574.3_6	585.1_1	580.2_9
42.00	574.3_5	585.2_2	580.3_1
43.02	574.3_2	585.2_4	580.2_8
44.00	574.3_3	585.2_4	580.3_6
45.00	574.3_0	585.2_8	580.3_3
46.00	574.2_6	585.3_3	580.3_0
47.00	574.2_7	585.3_5	580.3_2
48.00	574.2_5	585.4_0	580.3_6
49.00	574.3_0	585.4_1	580.4_3
50.00	574.2_9	585.5_4	580.4_8
52.00	574.2_2	585.8_4	580.5_3
55.00	574.2_2	585.9_5	580.6_0
60.00	574.1_5	586.3_1	580.7_7
20.00	576.30	585.1	581.8_5
$\left(\frac{\partial \pi_8}{\partial T}\right)_{>47^\circ} - \left(\frac{\partial \pi_8}{\partial T}\right)_{<42^\circ}$	0.075	0.100	0.080 mV/°C.

Table 4.

Cell	*P*	*T*	*R*	*U*	*S*
g CsCl/100 g H_2O	42.4	31.4	21.9	11.0	NaCl, unsat.
Temp. °C.	E.m.f. in mV.				
20.00	577.0_4	569.8_5	562.3_3	552.7_5	529.2_7
30.00	576.1_5	568.9_3	560.5_3	551.1_5	530.2_7
40.00	575.4_9	567.8_4	559.1_6	549.6_5	531.6_0
43.50	575.2_8	567.6_6	558.7_3	549.3_3	532.0_2
47.03	575.2_9	567.4_0	558.5_2	548.9_1	532.7_7
50.50	575.3_0	567.2_6	558.3_1	548.6_2	533.3_0
55.00	575.2_3	567.1_9	558.0_6	548.2_5	533.9_0
60.00	575.2_8	567.1_9	557.9_0	547.8_5	534.5_4
20.00	577.4_4	570.2	562.8_3	552.2	529.2_0
$\left(\frac{\partial \pi_8}{\partial T}\right)_{>47°} - \left(\frac{\partial \pi_8}{\partial T}\right)_{<42°}$	0.085	0.085	0.095	mV/°C.	

Table 5.

Cell.	A NaCl, sat.
Temp. °C.	E.m.f. in mV.
18.60	529.0_0
25.60	530.0_0
30.00	530.5_7
36.98	531.5_0
44.92	532.5_5
46.40	532.7_5
47.05	532.8_3
47.40	532.8_5
49.00	533.0_5
54.62	533.7_6
56.40	533.9_4
	B NaCl, sat.
18.40	529.0_3
26.45	530.0_5
35.40	531.2_4
41.26	532.0_4
50.26	533.1_8

on cells of Type (5) and on one cell with $CsPb_2Cl_5$ instead of $CsPbCl_3$ are also reproduced in this graph. The potentials of the latter cells show a smooth or linear dependence on the temperature without irregularities, but

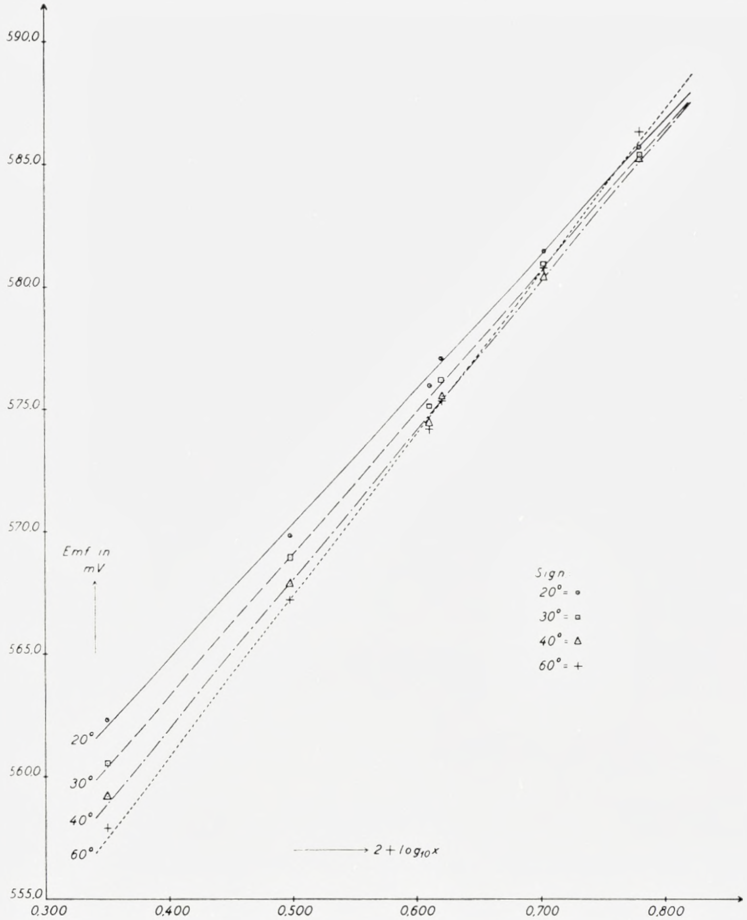

Fig. 4. The potential π_8 as a function of $\log_{10} x$, for given temperatures; x is the ionic mole fraction of Cl^- or Cs^+.

the former exhibit a rather sharp (though continuous) change in the temperature region from about 40°C. to about 50°C. As the slope, too, changes continuously it is seen from (12) that the entropy function is continuous throughout the transition region as required for a second-order transition. It is interesting that the maximum variation of G and S appears to lie about

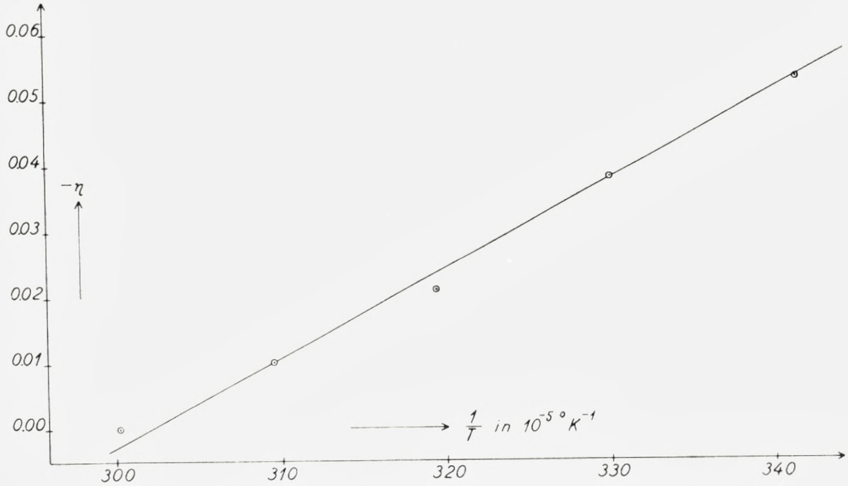

Fig. 5. η as a function of the reciprocal absolute temperature, $\frac{1}{T}$.

44°C., whereas from the crystallographic investigation one gets an impression that the maximum changes occur just below 47°C.

From the slopes of the linear parts of π_8, i.e. below 42°C. and above 47°C., values are obtained for $\left(\frac{\partial \pi_8}{\partial T}\right)_{>47^\circ} - \left(\frac{\partial \pi_8}{\partial T}\right)_{<42^\circ}$ for some selected CsCl-concentrations in the cells. They are given in the last line of Tables 3 and 4 and do not seem to vary systematically with the CsCl-concentrations. Nor would such a variation be expected on the assumption that the changes in π_8 have to be referred to changes in the chemical potential of the crystalline $CsPbCl_3$. From the mean value of these numbers we calculate the total change in entropy for the transition (3):

$$\Delta S = 4.0 \pm 0.3 \text{ cal/mol. degree} \qquad (19)$$

Discussion

The entropy change for a transition in the crystalline phase may be divided into two parts,[1] one of which originates from the changes in the configuration of the crystal, the other, called the "thermal entropy change", from changes in the frequency spectrum of the lattice vibrations. The *X*-ray analysis of $CsPbCl_3$ and $CsPbBr_3$[2] reveals practically no changes of the

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[1] See e.g. A.J. Dekker, *Solid State Physics*, p. 63. MacMillan 1958.
[2] Ref. 1 on page 4.

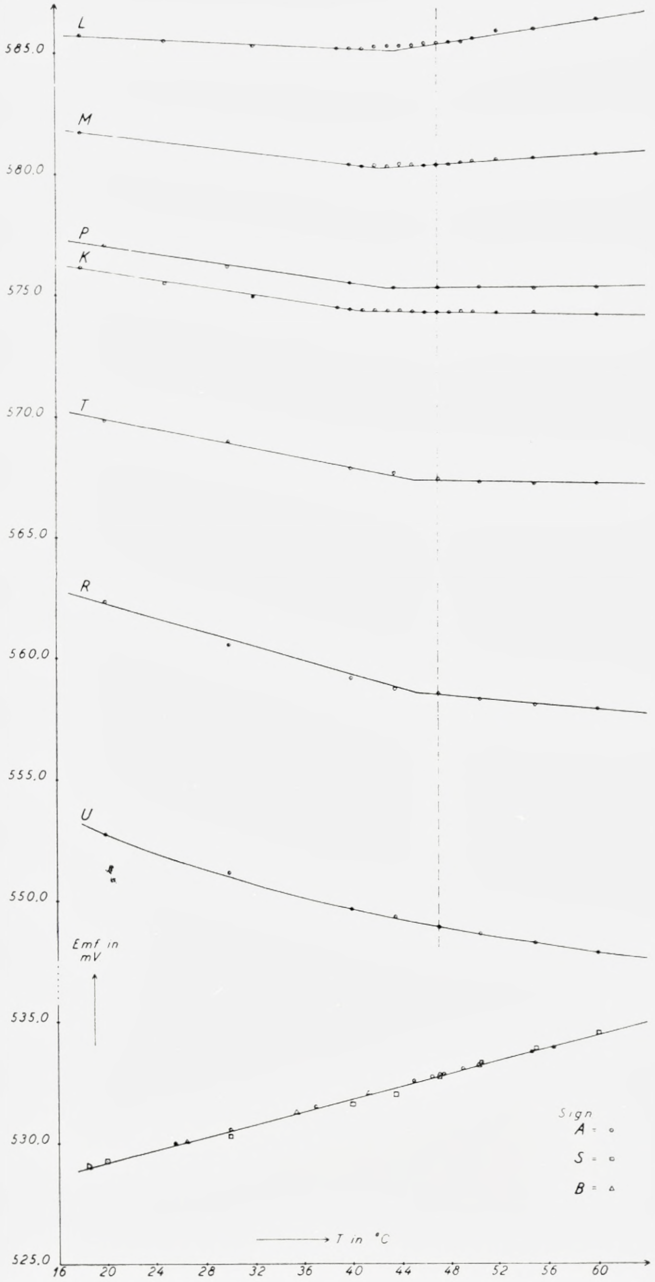

Fig. 6. Temperature variation of the electromotive forces for a number of cells with different electrolyte compositions. The letters refer to cells in the Tables 3, 4, and 5.

local atomic arrangements in these crystals during their respective transitions at 47°C. and 130°C., so that the lattice frequencies would be expected not to change very much here, and the vibrational or thermal contribution to the entropy may be considered unaltered. However, a superstructure which exists below the transition temperature, disappears above it, so that there must be a change in the configurational entropy. This change can be estimated as follows.

The axes of the primitive tetragonal unit cell all appear, from the *X*-ray analysis, to be twice as long as those of the cubic cell. As there is only one $CsPbX_3$-"molecule" in the latter, there must therefore be $2\times2\times2 = 8$ "molecules"—having different relative orientations—in the former. These eight situations for a $CsPbX_3$-unit in the tetragonal lattice become equivalent in the cubic structure because of transformation from one to the others, thus giving the latter an eight times larger thermodynamic probability than the former. (For a certain $CsPbX_3$-unit, which in the tetragonal crystal can have only one stable "configuration", there exist eight equivalent possibilities in the cubic crystals).

From BOLTZMANN's relation we therefore get:

$$\varDelta S = R \log 8 = 4.11 \text{ cal/mol. degree.} \tag{20}$$

The agreement of this with the experimental value obtained above lends some support to the interpretation given here.

Similar considerations would seem to apply to the transition observed in $BaTiO_3$ at 120°C.[1]. However, as the primitive, non-centrosymmetric unit cells below this temperature all have the same orientation, a strong electric polarization results, which gives a temperature-dependent, electrical contribution to the free energy. Above the transition the additional field is destroyed. It then follows that the observed entropy change $\varDelta S = -\left(\frac{\partial \varDelta G}{\partial T}\right)_p =$ 0.12 cal/mol. deg. may not be entirely due to change of the "configurational" entropy, but contains other contributions as well.

If in $BaTiO_3$-crystals the ions could occupy several close-lying potential minima these would be so close together that the barriers separating them would be very low and much narrower than in the $CsPbX_3$-crystals. Transitions to vibration states above or close to the barrier height may then easily occur at temperatures as low as 120°C., these minima thus losing their individuality, and there will be practically no configurational entropy change. (Compare the fact that the entropy of mixing for gases becomes

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[1] Ref. 1 on page 3.

zero when the molecules to be mixed become identical). Nor will the vibrational entropy change drastically.

If the transition observed at 47°C. in $CsPbCl_3$ corresponded to a change from vibrational rotation to free rotation of the Cl- or Cs-ions, then, following FRENKEL[1] $C_p = T\left(\frac{\partial S}{\partial T}\right)_p$ immediately after the transition should be lower than before it sets in. This would imply that the second derivative of the π_8-versus-T curves after 47°C. should be smaller than before, say, 42°C. No such change is indicated in the curves, but our measurements may not be accurate enough to show it. Further investigations of the transition by means of Raman- or infrared spectroscopy would appear interesting.

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[1] Ref. 3 on page 3.

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