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

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Synopsis

The cesium halide concentrations for which Cs_4PbX_6 and CsPbX_3 ($X = \text{Cl}$ 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 $\text{CsPbCl}_3(\text{tetragonal}) \rightarrow \text{CsPbCl}_3(\text{cubic})$. The value thus obtained is $\Delta S = 4.0$ cal/mol. degree. On the assumption that the process is essentially an order-disorder transformation, 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 .

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 EHRENFEST² 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.

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 parallelism 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.

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 $\text{Cs}_4\text{PbX}_6 \rightleftharpoons \text{CsPbX}_3 + 3\text{CsX}(\text{aq.})$ 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.

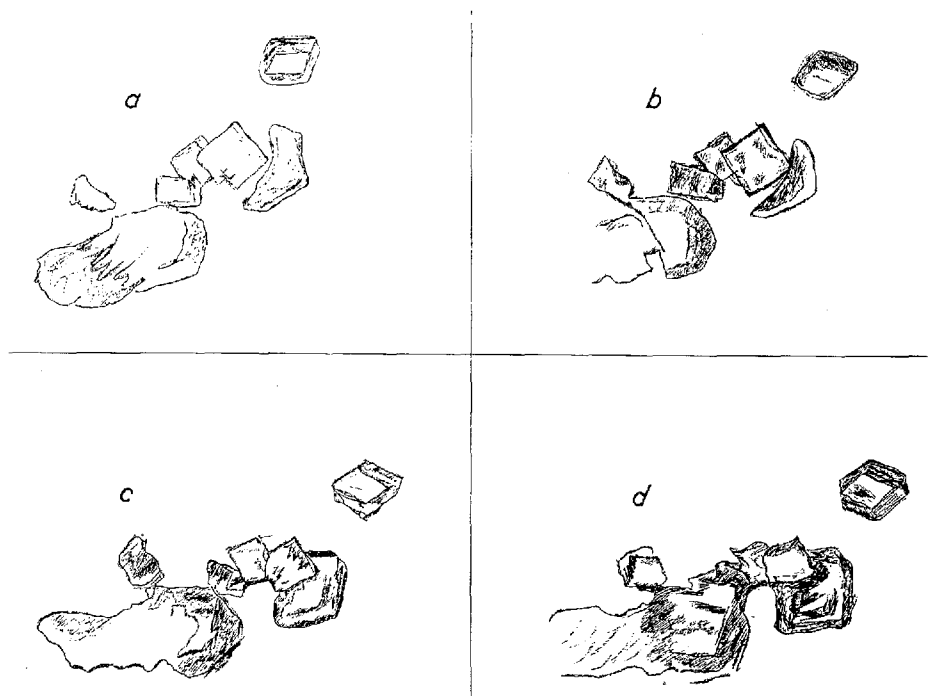


Fig. 1. Crystals of Cs_4PbCl_6 (rhombohedral) and CsPbCl_3 (cubic) in equilibrium with a CsCl -solution at different temperatures (drawn by means of an Abbe's drawing apparatus; magnification $100\times$).

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 $\pm 2^\circ\text{C}$. 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 caesium 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 $\text{Pb}(\text{NO}_3)_2$ (Merck, "rein") and very pure HX , and recrystallized several times from hot, dilute solutions of HX ($\text{pH} \approx 1$).

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 $120^\circ\text{C}.$) weighed samples of the solutions and then weighing the residues again.

As attainment of the equilibrium $2\text{CsPbX}_3 \rightleftharpoons \text{CsPb}_2\text{X}_5 + \text{CsX}(\text{aq.})$ 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^+		
$\text{Cs}_4\text{PbCl}_6 \rightleftharpoons \text{CsPbCl}_3 + 3\text{CsCl} \dots\dots$	151	$12.2_0 \cdot 10^{-2}$	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	
$2\text{CsPbCl}_3 \rightleftharpoons \text{CsPb}_2\text{Cl}_5 + \text{CsCl} \dots\dots$	20	$2.0_5 -$	$t_e \approx 58^\circ$	
	15	$1.5_3 -$	20	
$\text{Cs}_4\text{PbBr}_6 \rightleftharpoons \text{CsPbBr}_3 + 3\text{CsBr} \dots\dots$	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	
$2\text{CsPbBr}_3 \rightleftharpoons \text{CsPb}_2\text{Br}_5 + \text{CsBr} \dots\dots$	23.5	$1.9_1 -$	$t_e > 20^\circ$	
	20.5	$1.6_8 -$	20	
	18.8	$1.5_4 -$	$(t_e < 20^\circ)$	

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

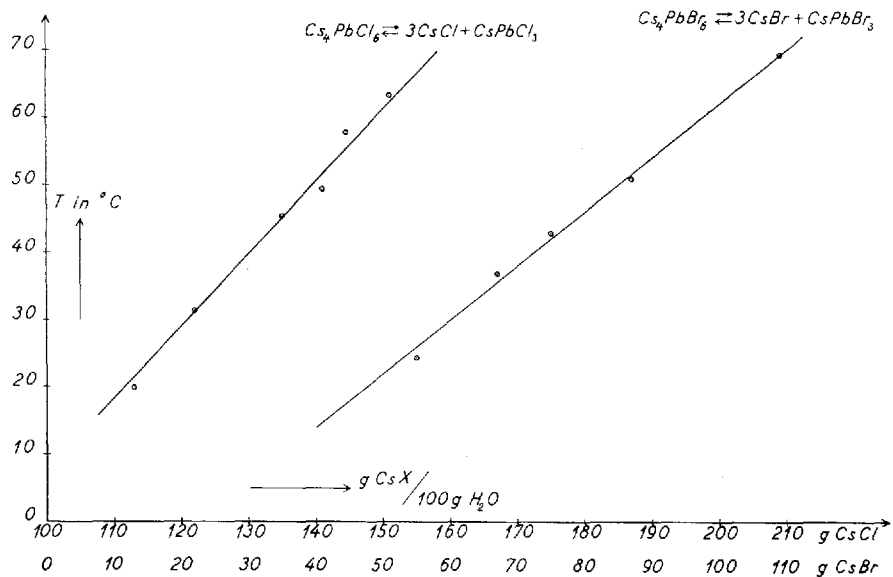


Fig. 2. The equilibrium temperature for $\text{Cs}_4\text{PbX}_6 \rightleftharpoons \text{CsPbX}_3 + 3\text{Cs}^+ + 3\text{X}^-$ as a function of the aqueous CsX -concentration.—The lower horizontal scale refers to CsBr , the upper one to CsCl .

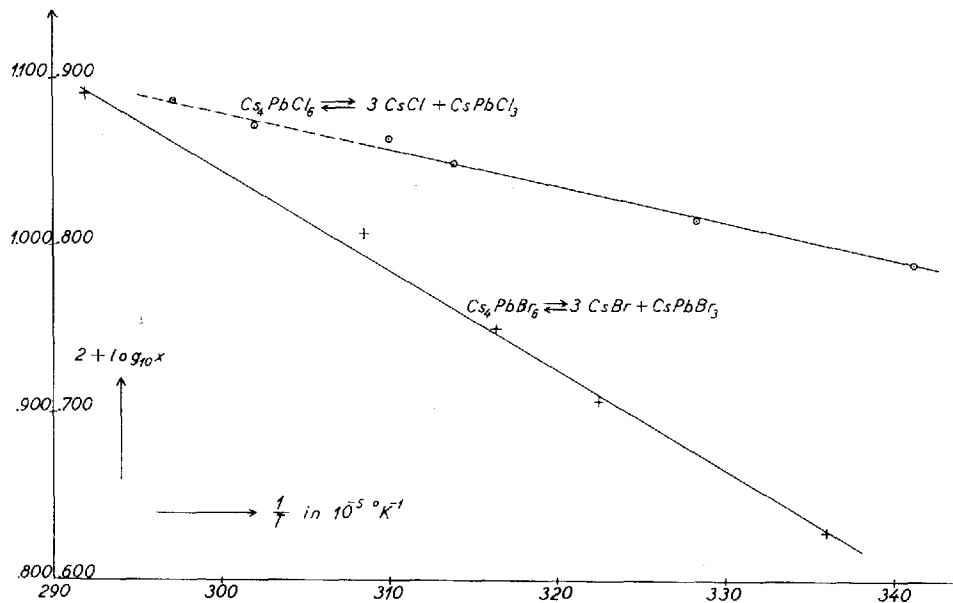
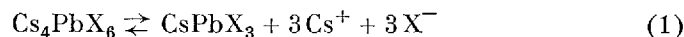


Fig. 3. $\text{Log}_{10} x_c$ as a function of the inverse equilibrium temperature in $^{\circ}\text{K}$. The left ordinate scale refers to CsCl , the right to CsBr .

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

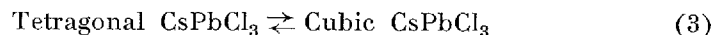


can be established, depend linearly on the temperature. If we neglect the temperature dependence of the chemical potentials of the crystalline solids and of the activity coefficients for CsX in solution we can estimate the heat of reactions for the above processes from VAN'T HOFF's relation expressed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

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

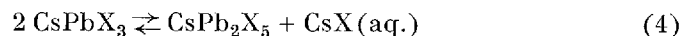
where x_e is the ionic mole fraction of Cs^+ or Cl^- at the equilibrium (1). These estimates, which should not be considered very accurate, are given in the last column of Table 1.

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



from measurements of ΔH for (1) above as well as below the transition temperature ($47^\circ\text{C}.$) for (3). Unfortunately it becomes increasingly difficult to obtain reliable values for the CsCl-concentrations as functions of the temperature above $55^\circ\text{C}.$ 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



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 $\text{X} = \text{Br}$.²

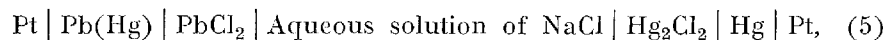
¹ Cf. H.M. POWELL and H.S. TASKER, *J. Chem. Soc.* London, 1937, p. 119 and Ref. 1 on page 7.

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

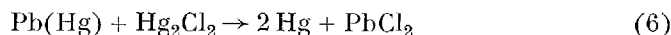
In this region we also have seen crystals which closely correspond to the characteristics given by WELLS: They were white, needle-shaped, showed parallel extinction, and on heating to 140–150°C. they turned orange-coloured. But it looks as if also CsPbCl_3 is dimorphous: Occasionally white needle-shaped 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 $X = \text{Cl}$. 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 -crystals¹ and thus represent one of the stages in changing the Pb -coordination.

Principle of the Electrochemical Determination of the Entropy Change

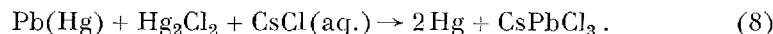
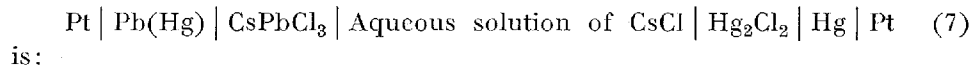
Let us consider an electrochemical cell of the type



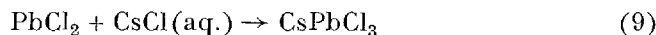
where Pb(Hg) denotes a Pb -amalgam saturated with Pb . The chemical process when two faradays flow from the left to the right is:



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



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



and

$$\pi = \pi_6 - \pi_8 = \frac{1}{2F} \left\{ \mu(\text{CsPbCl}_3) - \mu(\text{CsCl, aq.}) - \mu(\text{PbCl}_2) \right\}, \quad (10)$$

or

$$\mu(\text{CsPbCl}_3) = 2F\pi + RT \log_e \left\{ a(\text{CsCl, aq.}) \right\} + \mu(\text{PbCl}_2) + \mu_0(\text{CsCl, aq.}), \quad (11)$$

¹ Cf. Ref. 1 on page 7.

where $\mu_0(\text{CsCl, aq.})$ 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 $\mu(\text{PbCl}_2)$ and $\mu(\text{CsCl, aq.})$ 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 .:

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

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.

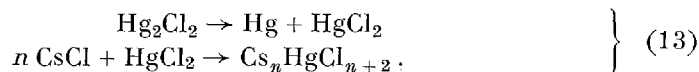
The quality of the chemicals were as follows: Hg, cleaned in dilute nitric acid and distilled in vacuum; Pb-amalgam (always containing solid phase) made from distilled Hg and Merck's Pb pro analysi. Other Pb-compounds were prepared as mentioned above. Except for preliminary experiments, where rather 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:



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 CsPb₂Cl₅ instead of CsPbCl₃.

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

$$\pi_8 = \beta \log_{10} x + b. \quad (14)$$

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

$$\pi_8 = 2.3026 \cdot \frac{RT}{F} \log_{10}(xf_{\pm}) + a = \alpha \log_{10}(xf_{\pm}) + a. \quad (15)$$

From ROBINSON and STOKES's tables of activity coefficients¹ 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:

$$\eta = \frac{\beta - \alpha}{\alpha} \quad (16)$$

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

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 ₆
— 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 ₅	530.1 ₅
-----	—	576.1 ₅	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. GÜNTEMBERG¹ 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:

$$\log_{10} f_{\pm} = \eta \log_{10} x + \sigma, \quad (17)$$

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 SCHUPP² 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 .

¹ E. GÜNTEMBERG, *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 H₂O to the CsCl-concentrations considered may be obtained from

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

We find $Q \approx -R \cdot 2.303 \cdot 135 \cdot \log_{10}(x)$ which for a 2 molal CsCl-solution becomes $Q \approx 900$ 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	<i>K</i>	<i>L</i>	<i>M</i>
g CsCl/100 g H ₂ O	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 ₀	—
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	<i>P</i>	<i>T</i>	<i>R</i>	<i>U</i>	<i>S</i>
g CsCl/100 g H ₂ O	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 ₈	560.5 ₈	551.1 ₆	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 ₂	552.2	529.2 ₀
$\left(\frac{\partial \pi_s}{\partial T}\right)_{>47^\circ} - \left(\frac{\partial \pi_s}{\partial T}\right)_{<42^\circ}$	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

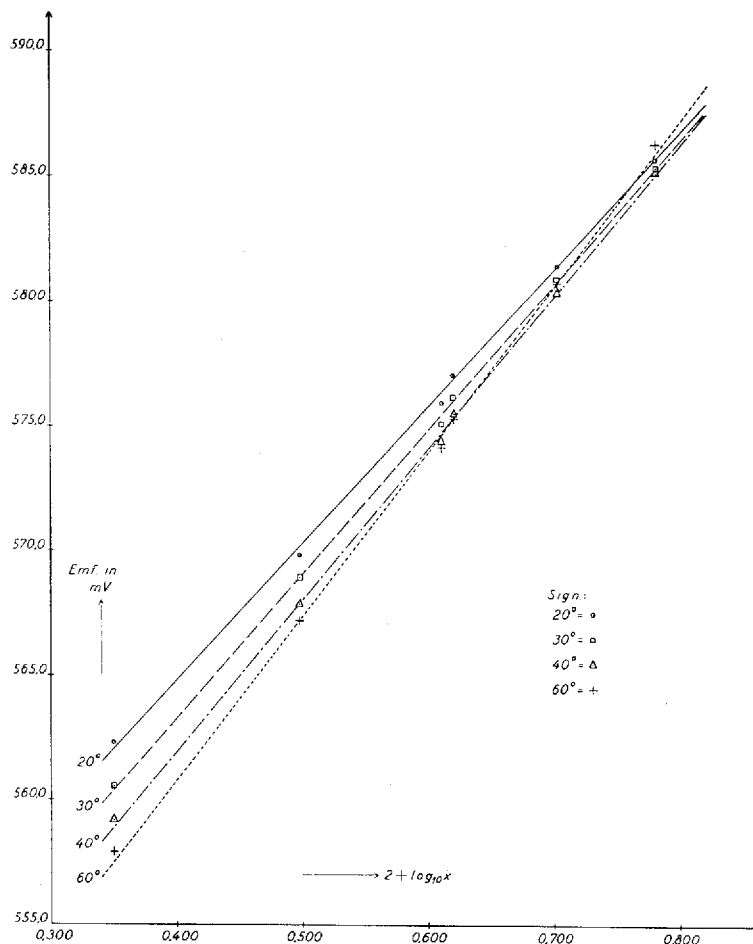


Fig. 4. The potential π_8 as a function of $\log_{10} x$, for given temperatures; x is the ionic mole fraction of Cl^- or Cs^+ .

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

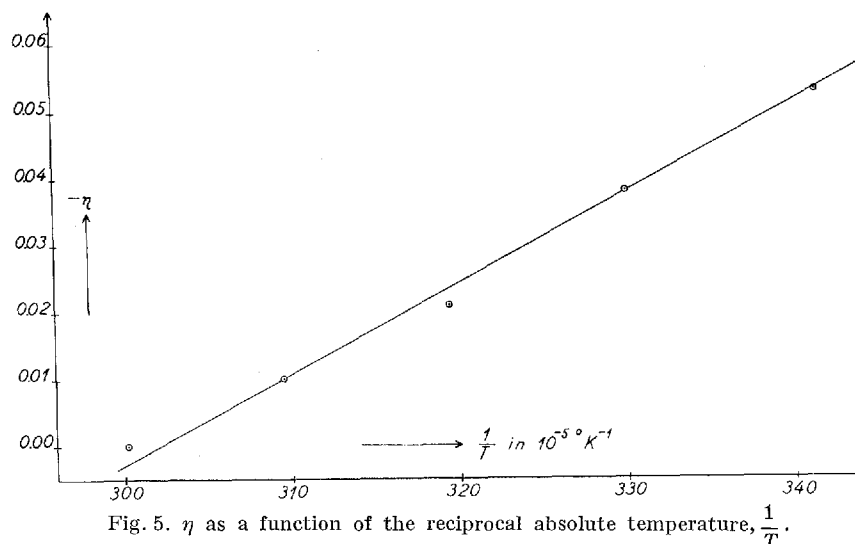


Fig. 5. η as a function of the reciprocal absolute temperature, $\frac{1}{T}$.

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 CsPbCl₃. From the mean value of these numbers we calculate the total change in entropy for the transition (3):

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

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 CsPbCl₃ and CsPbBr₃² reveals practically no changes of the

¹ See e.g. A.J. DEKKER, *Solid State Physics*, p. 63. MacMillan 1958.

² Ref. 1 on page 4.

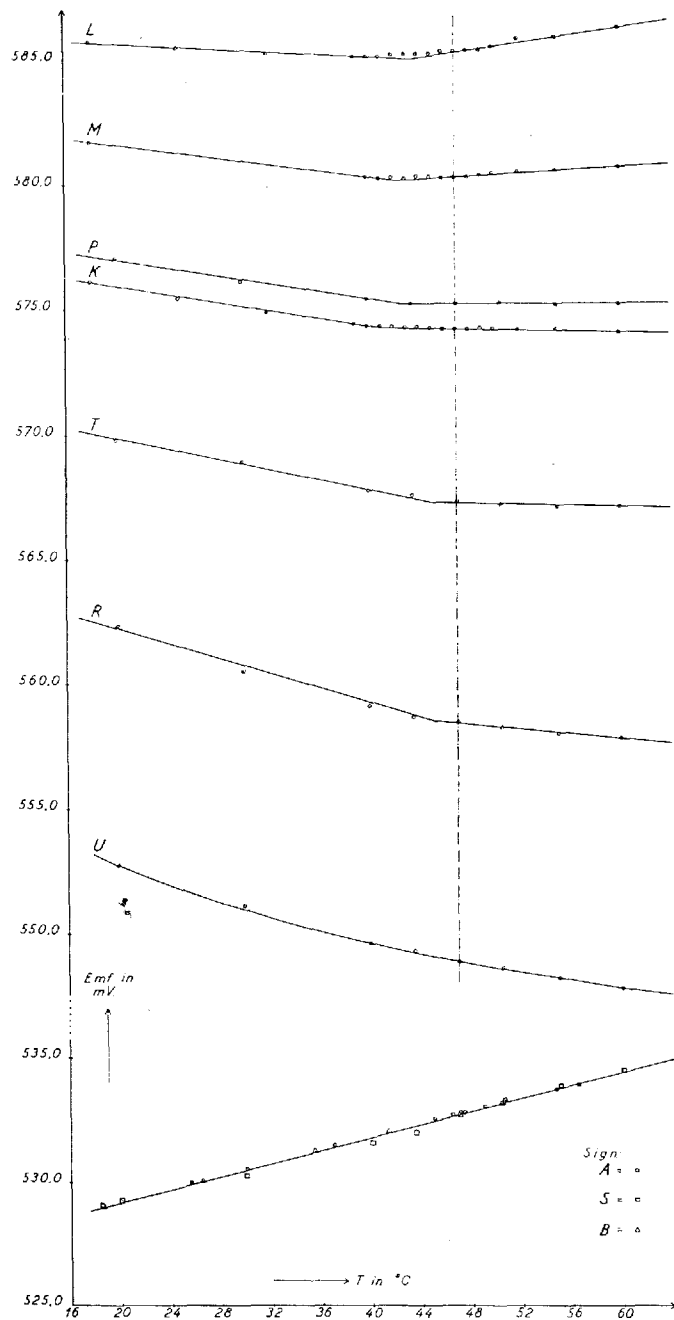


Fig. 6. Temperature variation of the electromotive forces for a number of cells with different electrolyte compositions. The letters refer to cells in the Tables 3, 4, and 5.

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 $2 \times 2 \times 2 = 8$ “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:

$$\Delta S = R \log 8 = 4.11 \text{ cal/mol. degree.} \quad (20)$$

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 $\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_p = 0.12 \text{ cal/mol. deg.}$ 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

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 CsPbCl₃ corresponded to a change from vibrational rotation to free rotation of the Cl- or Cs-ions, then, following FRENKEL¹ $C_p = T \left(\frac{\partial S}{\partial T} \right)_p$ 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.

