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PHYSICAL PROPERTY MEASUREMENTS ON CESIUM CHLORIDE AND
CESIUM CHLORIDE-ALKALI METAL CHLORIDE SYSTEMS

by

H. T. Fullam

Chemical Systems Technology Section
Chemical Technology Department

Supported by
Atlantic Richfield Hanford Company

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1. INTRODUCTION

In the waste management program at Hanford fission product cesium is to be separated from aged wastes and packaged as cesium chloride in small high integrity containers. The physical properties of cesium chloride can affect the process used to load the CsCl into the containers and can influence the design of the containers. In turn, the purity of the cesium chloride can affect its physical properties. It is necessary, therefore, to know the properties of the CsCl as a function of product purity in order to develop the packaging process. In this study several properties of CsCl were studied as a function of purity including the solid phase transition, thermal expansion, melting point, and adsorption of water. The compaction of CsCl by step pressing was also evaluated. The results of these studies are summarized in this report.

2. SUMMARY

The cesium chloride produced in the Atlantic Richfield Hanford Company (ARHCO) waste packaging plant may contain substantial amounts of sodium chloride and potassium chloride. This contamination can affect the physical properties of the CsCl. In this study several properties of CsCl were measured and the effect of NaCl and KCl additions on each determined.

The phase diagrams for the systems CsCl-KCl, CsCl-NaCl, and CsCl-KCl-NaCl were determined. The melting point of pure CsCl was determined to be 645 °C. The CsCl-KCl system shows a minimum melting point of 605 °C at a KCl content of 19.2 wt%. The CsCl-NaCl system shows an eutectic of 493 °C at 15.5 wt% NaCl. In the ternary system a minimum melting point of 478 °C was found at a composition of 68 wt% CsCl-17 wt% KCl-15 wt% NaCl.

Pure cesium chloride undergoes a phase transition, on heating, which begins at 475 °C. When KCl is added the temperature at which the phase transition begins drops sharply. For a CsCl system containing greater than 20 wt% KCl the phase transition initiates below 315 °C. The addition of NaCl to CsCl causes only a slight drop in the phase transition temperature. In the ternary system CsCl-KCl-NaCl the phase transition temperature decreases sharply as the CsCl content is decreased.

Additions of NaCl and/or KCl to CsCl causes the thermal expansion coefficient (below the phase transition) of the system to decrease. The linear expansion due to the phase transition is almost directly proportional to the CsCl in the system.

The presence of impurities can have a pronounced effect on the properties of CsCl; and these effects must be considered when designing the container which is to be used for packaging the CsCl.

3. CESIUM CHLORIDE PURITY

It is anticipated that the cesium chloride prepared in the Waste Packaging Plant may contain as much as 10 wt% impurities. It is further anticipated that sodium chloride and potassium chloride will be the major impurities with lesser amounts of other materials present (i.e. rubidium chloride and corrosion products). Studies have been made to measure several of the physical properties of CsCl and to determine the effect of sodium chloride and potassium chloride additions on some of these properties. The results of the studies are presented in the following sections.

4. PHASE DIAGRAM DETERMINATIONS4.1 Melting Point of Cesium Chloride

Reported values for the melting point of pure CsCl vary over a wide range as shown by the data presented in Table I.

TABLE I. The Melting Point of Cesium Chloride

<u>Value, °C</u>	<u>Reference</u>	<u>Value, °C</u>	<u>Reference</u>
629	1	645	6
630	2	646	7
638	3	647	8
640	4	648	9
643	5	649	10

An average value for the melting point, based on 18 reputable literature values, appears to be about 645 °C. In this work the melting point of CsCl was determined in two ways: by differential thermal analysis and by the thermal arrest method. A DuPont Model 900 Differential Thermal Analyzer was used for the DTA studies. The thermal arrest measurements were obtained in the standard fashion using porcelain or quartz crucibles, calibrated chromel-alumel thermocouples, and a Moseley X-Y recorder. The cesium chloride used in the work was obtained from Varlacoid Chemical Company and had a reported purity of 99.9+. Emission and spark source mass spectroscopy verified the purity value.

Good agreement was obtained between the two methods. A melting point for CsCl of 644 ± 3 °C was obtained by differential thermal analysis (DTA) based on twenty measurements. The thermal arrest method gave a melting point of 646 ± 2 °C based on twelve measurements. Based on the two methods, the melting point of CsCl is taken as 645 °C.

4.2 CsCl-KCl Binary System

The phase diagram for the binary system CsCl-KCl was studied over the entire composition range. The two salts form a solid solution having a minimum melting point. Thermal arrest and DTA measurements were used to determine the various points in the diagram. The phase diagram obtained is shown in Figure 1. The system has a minimum melting point of 605 °C at a KCl content of 19.2 wt%. The area of the diagram of particular interest (0-10 wt% KCl) is shown in Figure 2. The diagram differs from those reported by Dombrovskaya⁽¹¹⁾ and Zhemchuzhni⁽⁷⁾ in that the minimum melting point obtained in this study is 10-25 °C lower than those previously reported. Our value does agree quite closely with the value of 606 °C reported by Ilyasov⁽¹²⁾ who studied the CsCl-KCl-NaCl ternary.

4.3 CsCl-NaCl Binary System

The phase diagram for the binary system CsCl-NaCl was also determined over the entire composition range using thermal arrest, DTA, and x-ray analysis. The results obtained are presented in Figure 3. The system has a eutectic at 15.5 wt% NaCl with a melting point of 493 °C. The two salts do not form a solid solution, and below 493 °C the system consists of two solid phases. However, there does appear to be a slight solubility of NaCl in solid CsCl.

The phase diagram obtained is similar to that reported by Samuseva⁽⁹⁾ except in the 20-75% NaCl portion of the diagram where the liquidus line varies significantly from that reported by Samuseva. Samuseva's data are shown in Figure 3 by the dashed line. The 0-10 wt% NaCl portion of the diagram is shown in Figure 4.

4.4 CsCl-KCl-NaCl Ternary System

The phase diagram for the ternary system CsCl-KCl-NaCl was studied over the entire composition range with emphasis on that area of the diagram containing >90 wt% CsCl. The diagram obtained is presented in Figures 5 and 6. It is very similar to that reported by Ilyasov⁽¹²⁾ except in the low CsCl portion of the diagram. In this study it was found that the ternary has a minimum melting point of 478 ± 3 °C at a composition of 68 wt% CsCl - 17 wt% KCl - 15 wt% NaCl. Ilyasov reports a minimum melting point of 480 °C at 68.1 wt% CsCl - 16.3 wt% KCl - 15.6 wt% NaCl. The only major difference in the two diagrams is the minimum melting point for the NaCl-KCl binary. Ilyasov reported a temperature of 658 °C. We obtained a value of 646 ± 4 °C (which agrees with the value of 645 ± 2 °C reported by Coleman and Lacy⁽¹³⁾). The difference in the two values changes the position of the isotherms slightly in the low CsCl area of the phase diagram.

5. PHASE TRANSITION MEASUREMENTS

5.1 Phase Transition of Cesium Chloride

Pure cesium chloride undergoes a phase transition on heating from the low temperature CsCl structure (cubic) to a high temperature sodium chloride structure (face-centered cubic).

The phase transition has been reported to occur at 469 °C.⁽¹⁴⁾ In this study the phase transition temperature was determined by differential thermal analysis and thermal expansion measurements using the DuPont Model 900 Differential Thermal Analyzer and Thermomechanical Analyzer accessory. Typical DTA and thermal expansion data for 99.9+% CsCl are shown in Figure 7. DTA data gave a value of 474 ± 3 °C for the temperature at which the phase transition starts. Thermal expansion measurements gave a value of 475 ± 2 °C. The phase transition, on heating, is not instantaneous, and when the CsCl sample is heated at a finite rate the phase transition takes place over a substantial temperature range. Figure 8 presents several thermal expansion curves for a CsCl sample heated at different rates and shows that the faster the heating rate the greater the temperature range over which the transition occurs.

When the high temperature form of CsCl is cooled the reversion to the low temperature form occurs at approximately the same rate as on heating. Figure 9 shows a typical expansion and contraction curve for pure CsCl.

5.2 Phase Transition of the CsCl-KCl System

When KCl is added to CsCl the temperature at which the phase transition starts is decreased greatly. The rate at which the phase transition occurs on heating is also decreased. More important, however, is the fact that the rate of phase transition on cooling is decreased very significantly so that with finite cooling rates (>0.5 °C/min) very little reversion occurs on cooling a CsCl-KCl sample. It is necessary to anneal the sample

at 250-300 °C for substantial periods of time (>4 hours) to insure complete reversion of the CsCl to the low temperature form. X-ray diffraction patterns obtained at room temperature with unannealed samples, containing 1-5 wt% KCl, showed a mixture of the low temperature and high temperature forms of CsCl was present.

Figure 10 shows how the temperature at which the phase transition starts decreases as the KCl content increases. Fair agreement was achieved between DTA and thermal expansion measurements. The phase transition was detected for samples containing as much as 90 wt% KCl. However, the temperature at which the transition starts is poorly defined for samples containing over 50 wt% KCl. Additional work is needed to determine accurately the phase transition temperatures for samples high in KCl.

The rate at which the phase transition occurs, on heating, depends on the KCl content. Figure 11 shows the thermal expansion curves for CsCl-KCl samples of various compositions, all of which were heated at the same rate. It is difficult to obtain a precise measure of the rate of transition. However, from the curves presented in Figure 11 it is readily apparent that the temperature range over which the transition occurs increases as the KCl content of the binary increases.

When a CsCl-KCl sample is cooled, the reversion to the low temperature form is inhibited by the KCl. For example, Figure 12 shows DTA and thermal expansion-contraction plots for annealed samples of CsCl-10 wt% KCl. The phase transition on heating is readily apparent on both the DTA and expansion

curves. Upon cooling, however, it is impossible to detect the phase transition by DTA, and only a slight indication of the transition is observed in the thermal contraction curve. If a CsCl-KCl sample is reheated after rapid cooling (>10 °C/min) it is impossible to detect a phase transition by DTA, although a slight transition can be detected by the thermal expansion procedure.

5.3 Phase Transition of the CsCl-NaCl System

It has been reported that in the CsCl-NaCl system two solid phases form below the eutectic temperature of 493 °C with no solid solution.⁽⁹⁾ If this is true then the phase transition temperature for CsCl should be unaffected by the addition of NaCl. In this study, however, it was found that the temperature at which the transition starts decreased slightly with the addition of NaCl (see Figure 13). This indicates there is probably a slight solubility of NaCl in solid CsCl.

It was impossible to obtain good thermal contraction curves for the CsCl-NaCl system because of the low eutectic temperature (493 °C). In all cases the sample began to melt before the phase transition was complete on heating. DTA data showed that the phase transition occurred on cooling regardless of the cooling rate. However, the temperature at which the phase transition started was substantially lower than the temperature at which the transition began on heating. Figure 14 shows the results obtained with a CsCl-3 wt% NaCl sample. Other CsCl-NaCl compositions showed a similar lowering of the transition temperatures on coolings. However, it was impossible to correlate the temperature lowering with composition. If the thermal expansion runs were stopped before the phase transition was

complete (and before the eutectic temperature was reached) the sample could be cooled and a thermal contraction curve obtained. Figure 15 shows such a curve for a CsCl-10 wt% NaCl sample. It is interesting to note that even though the phase transition was incomplete when cooling was started the phase reversion did not begin until the temperature had dropped approximately 60 °C. This temperature was at least 25 °C below where the phase transition had started on heating.

5.4 Phase Transition of the CsCl-KCl-NaCl System

The CsCl-KCl-NaCl system is quite complex. The phase transition was detected on heating for all compositions containing ≥ 10 wt% CsCl. As with the CsCl-KCl system, however, samples must be annealed to assure complete reversion to the low temperature form on cooling. The temperature at which the phase transition starts, on heating, depends on the composition but the exact relationship is very complex. In the ternary system, NaCl acts almost like KCl in its effect on the phase transition temperature. This can be seen by referring to the data presented in Table II. For the ternary system, it is best to assume that the NaCl is KCl and that the phase transition will occur as shown in Figure 10.

TABLE II. Phase Transition Data For CsCl-KCl-NaCl System

Composition, wt%			Start of Phase Transition, °C
CsCl	KCl	NaCl	
95	5	0	340
95	4	1	343
95	3	2	340
95	2	3	338
95	1	4	342
95	0	5	465
90	10	0	320
90	9	1	321
90	7	3	325
90	5	5	323
90	3	7	324
90	1	9	320
90	0	10	467

6. THERMAL EXPANSION DATA

6.1 Cesium Chloride

The thermal expansion of pure CsCl was determined from 25 °C through the phase transition (up to 540 °C). Expansion up to the phase transition temperature is almost linear with temperature. Figure 16 gives the value of the thermal expansion coefficient, α , as a function of temperature for CsCl. For this work, the thermal expansion coefficient will normally be reported as an average value for the temperature range 25-300 °C.

A value of 300 °C was selected as the upper limit because it is just below the minimum temperature at which the phase transition starts in the CsCl-KCl and CsCl-KCl-NaCl systems.

For pure CsCl, $\alpha_{25-300} \text{ } ^\circ\text{C}$ was determined to be $55.5 \times 10^{-6} / ^\circ\text{C}$ (based on ten determinations). This is in exact agreement with the value of $\alpha_{20-320} \text{ } ^\circ\text{C} = 55.5 \times 10^{-6} / ^\circ\text{C}$ reported by Whittemore. (15)

For the high temperature form of CsCl the thermal expansion coefficient between 500 and 540 °C was determined to be $\alpha_{500-540} \text{ } ^\circ\text{C} = 42.5 \times 10^{-6} / ^\circ\text{C}$, which was slightly lower than the value of $\alpha_{570-590} \text{ } ^\circ\text{C} = 51 \times 10^{-6} / ^\circ\text{C}$ reported by Christian and Lynch. (16)

At the phase transition, the linear expansion was calculated at the mid-point of the temperature range over which the transition occurs (see Figure 17). For pure CsCl the linear expansion at the phase transition was determined to be 5.4%. Since the two CsCl structures are cubic and isotropic, the volumetric expansion at the phase transition is the cube of the linear expansion. This gives a value of 17.1% for the volumetric expansion of CsCl due to the phase transition. This compares with a value of 16% reported by Menary, et.al. (14)

6.2 CsCl-Alkali Metal Chloride Systems

For the CsCl-KCl and CsCl-NaCl systems the value of $\alpha_{25-300} \text{ } ^\circ\text{C}$ decreases as the CsCl content of the system decreases. Figure 18 shows the relationship between $\alpha_{25-300} \text{ } ^\circ\text{C}$ and composition for the two systems. For pure KCl and pure NaCl, values for $\alpha_{25-300} \text{ } ^\circ\text{C}$ of $41.6 \times 10^{-6} / ^\circ\text{C}$ and $43.0 \times 10^{-6} / ^\circ\text{C}$ were obtained. These compare with values of $41.7 \times 10^{-6} / ^\circ\text{C}$ and $45.6 \times 10^{-6} / ^\circ\text{C}$ reported in the literature for $\alpha_{20-320} \text{ } ^\circ\text{C}$. (15)

The linear expansion at the phase transition for both the CsCl-NaCl and CsCl-KCl systems is almost directly proportional to the CsCl content of the system. Figure 19 shows how the linear expansion varies with composition for both systems.

All the thermal expansion data presented for the CsCl-KCl systems were obtained with samples which were melt cast and then fully annealed to insure complete reversion to the low temperature form. If the samples were not annealed it was impossible to obtain reproducible thermal expansion data. For example, when an unannealed CsCl-10 wt% KCl sample is heated, some high temperature phase material is initially present. When the temperature reached 200-300 °C the high temperature material partially reverts to the low temperature form. This results in an actual decrease in sample length (see Figure 20) even though the sample temperature is increasing. Such behavior makes it impossible to accurately determine the thermal expansion between 25 and 300 °C and at the phase transition without annealing. It was normally necessary to anneal the samples for several hours at 250-300 °C to insure complete reversion to the low temperature form.

With the CsCl-KCl-NaCl system it is also necessary to anneal the samples to obtain reliable thermal expansion data. Figure 21 shows how the thermal expansion from 25-400 °C for ternary samples varies with the annealing time (the expansion data presented in Figure 21 include the expansion due to the phase transitions). The data show that an annealing time of at least 4 hours at 275 °C is required to obtain complete reversion.

Linear expansion values between 25-300 °C for the various ternary compositions fall between those obtained for the two binary compositions of the same CsCl content (see Table III).

TABLE III. Thermal Expansion Of
CsCl-KCl-NaCl Mixtures

Composition, wt%			$\alpha_{25-300}^{\circ}\text{C}$
<u>CsCl</u>	<u>KCl</u>	<u>NaCl</u>	
90	10	0	48.0×10^{-6}
90	0	10	49.4×10^{-6}
90	5	5	48.5×10^{-6}
70	30	0	45.0×10^{-6}
70	0	30	46.3×10^{-6}
70	10	20	45.7×10^{-6}
70	15	15	45.5×10^{-6}
70	20	10	45.4×10^{-6}

In those cases where it is critical to know the maximum thermal expansion which may occur, it is best to assume all of the KCl and NaCl in the ternary is NaCl and take the thermal expansion value from the CsCl-NaCl curve in Figure 18.

At the phase transition, the expansion which occurs with the ternary system is dependent on the CsCl content, and the value can be taken from the binary data presented in Figure 19. For example, a sample containing 50 wt% CsCl-25 wt% NaCl-25 wt% KCl will have approximately the same linear expansion at the phase transition as one containing 50 wt% CsCl-50 wt% KCl or 50 wt% CsCl-50 wt% NaCl.

7. COMPACTION OF CESIUM CHLORIDE

High purity (99.9%) cesium chloride is readily compacted to high densities by cold pressing. Pellets of CsCl were pressed to >99% of theoretical density at pressures as low as 38 tons (TSI) per square inch. The theoretical density of CsCl at 25 °C was taken as 3.999 g/cm³.⁽¹⁷⁾ Cesium chloride powder prepared by the packaging plant flowsheet and which contained 3.5 wt% impurities compacted almost as readily as pure CsCl. Figure 22 shows the densities obtained when CsCl prepared by the flowsheet was cold pressed into pellets at various pressures. The densities were calculated from the physical dimension of the pellets.

When KCl or NaCl is added to pure CsCl and the mixture melted, solidified, and crushed the resultant powder is more difficult to press than pure CsCl. Figure 23 shows compaction data for various CsCl-KCl, CsCl-NaCl and CsCl-KCl-NaCl mixtures. The theoretical densities of the mixtures were taken as the arithmetic average of the individual components:

$$\text{Theoretical Density} = \frac{100}{\frac{\text{wt\% A}}{\text{Density of A}} + \frac{\text{wt\% B}}{\text{Density of B}}}$$

$$\text{Theoretical Density} = \frac{100}{\frac{\text{wt\% A}}{\text{Density of A}} + \frac{\text{wt\% B}}{\text{Density of B}} + \frac{\text{wt\% C}}{\text{Density of C}}}$$

8. ADSORPTION OF MOISTURE

When CsCl is exposed to atmospheric moisture it will adsorb the moisture at a relatively slow rate. Mixtures of CsCl and KCl and/or NaCl will adsorb atmospheric moisture at a more rapid rate. To make the measurements, samples of CsCl plus KCl and/or NaCl were melted, solidified, and crushed to -100 mesh. Samples of each powder were placed in open beakers and exposed to the atmosphere. The weight change, indicating pickup of water, was followed as a function of time. The results obtained are shown in Figure 24. Cesium chloride samples, prepared in the same fashion as the CsCl-NaCl-KCl mixtures, were also run as a standard for comparative purposes. The results show that the lower the CsCl content of the mixture the more rapid the adsorption of moisture.

9. CAPSULE DESIGN CONSIDERATIONS

The CsCl prepared in the packaging plant will be stored in small high integrity containers. Without external cooling the centerline of the container may reach a temperature as high as 400 °C. Under these conditions, impurities in the CsCl can have a significant effect on the condition of the chloride in the container. For example, if the CsCl in the container is at a temperature above 350 °C, and if the CsCl contains greater than 3 wt% KCl, then the CsCl will be in the high temperature form. Therefore, the capsule must be designed to allow for expansion of the CsCl to the high temperature form. If melt casting is used to fill the CsCl containers, thermal expansion would not be a problem. If the CsCl contains both KCl and NaCl then a molten phase will be present if the temperature of the salt exceeds 478 °C. This can have an effect on the compatibility of the salt with the container metal. In designing the CsCl

container it is necessary, therefore, to consider all of the effects which impurities will have on the properties of the CsCl.

10. ACKNOWLEDGEMENTS

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11. REFERENCES

1. H. Keitel. Neues Jahrb. Mineral Geol., A52, p. 420. 1955.
2. E. P. Dergunov, Dokl. Akad Nauk SSSR, 64 (4), p. 519. 1949.
3. A. Bernman and G. N. Maslennikova, Russian J. Inorg. Chem., p. 714. 1962. (Eng. Trans.).
4. In-Chzhu Sun and I.S. Morozov, Zhur. Neorg. Khim., 3, p. 916. 1958.
5. B. F. Markov, Zhur. Obshchei Khim., 25, p. 2042. 1955.
6. V. V. Safonov, et.al., Russian J. Inorg. Chem., P. 1022. 1962. (Eng. Trans.).
7. S. Zhemchuzhnui and F. Rambach, Z. Anorg. Chem., 65, p. 421. 1910.
8. B. F. Markov, et.al., Ukrain. Khim. Zhur., 22, p. 290. 1956.
9. R. G. Samuseva and V. E. Plyushchev, Russian J. Inorg. Chem., p. 1093. 1960. (Eng. Trans.).
10. B. G. Korshunov, et.al., Russian J. Inorg. Chem., p. 774. 1964. (Eng. Trans.)
11. O. S. Dombrovskaya, Zh. Obshch. Khim., 3, p. 1019. 1933.

12. I. I. Ilyasov and A. G. Bergman, Russian J. Inorg. Chem., p. 356 1962. (Eng. Trans.)
13. Coleman and Lacy. Mat. Res. Bull., 2, p. 935. 1967.
14. J. W. Menary, A. R. Ubbelohde and I. Woodward, Proc. Roy. Soc. (London), A208, p. 159. 1951.
15. D. Whittemore, Ceramic Bulletin, 41, p. 513. 1962.
16. J. M. Christian and D. W. Lynch, J. Chem. Phys., 40, p. 248, 1964.
17. J. W. Johnson, P. A. Argon, and M. A. Bredig, J. Am. Chem. Soc., 77, pp. 2734-7. 1955.

12. APPENDIX



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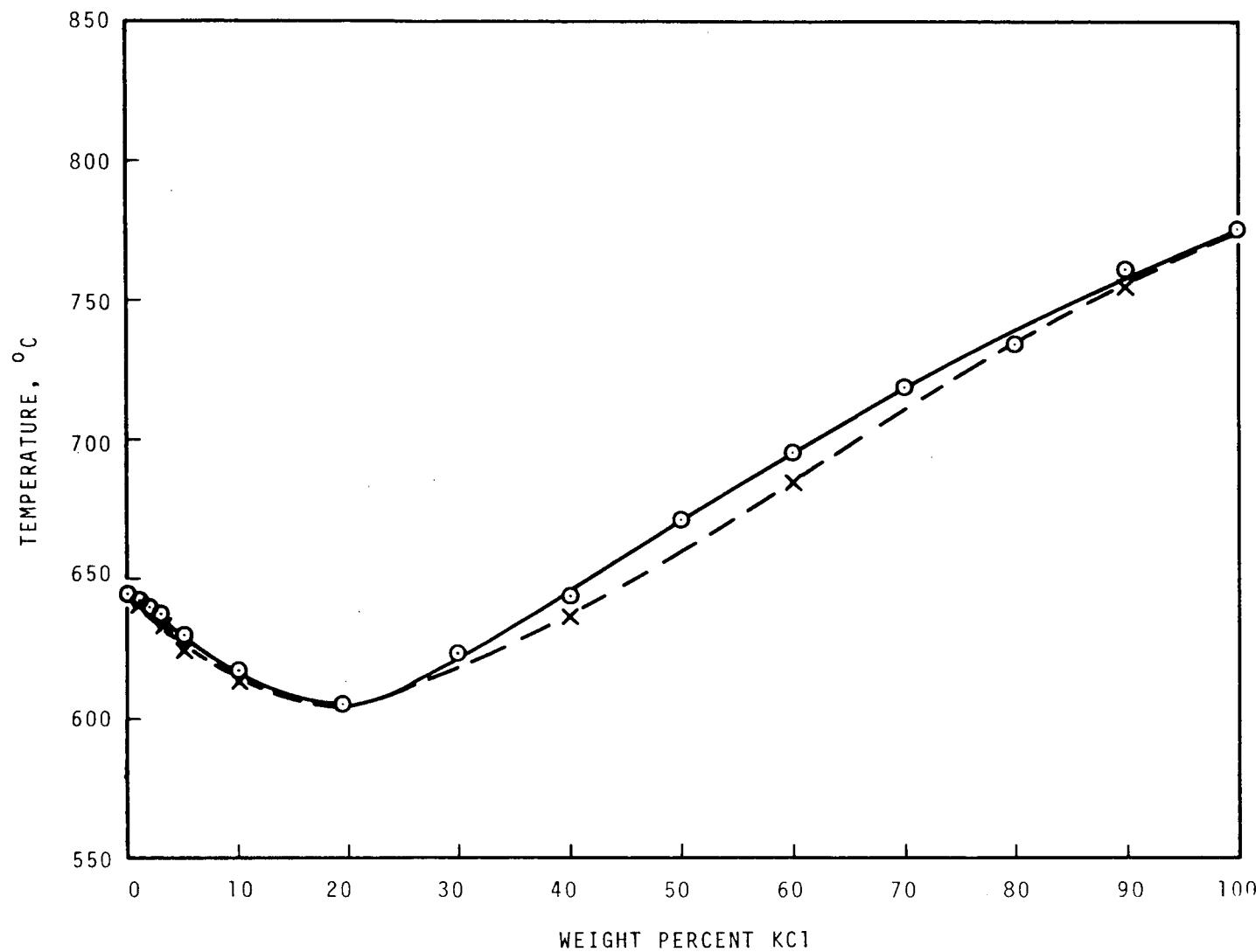


FIGURE 1 PHASE DIAGRAM FOR THE SYSTEM CsCl-KCl

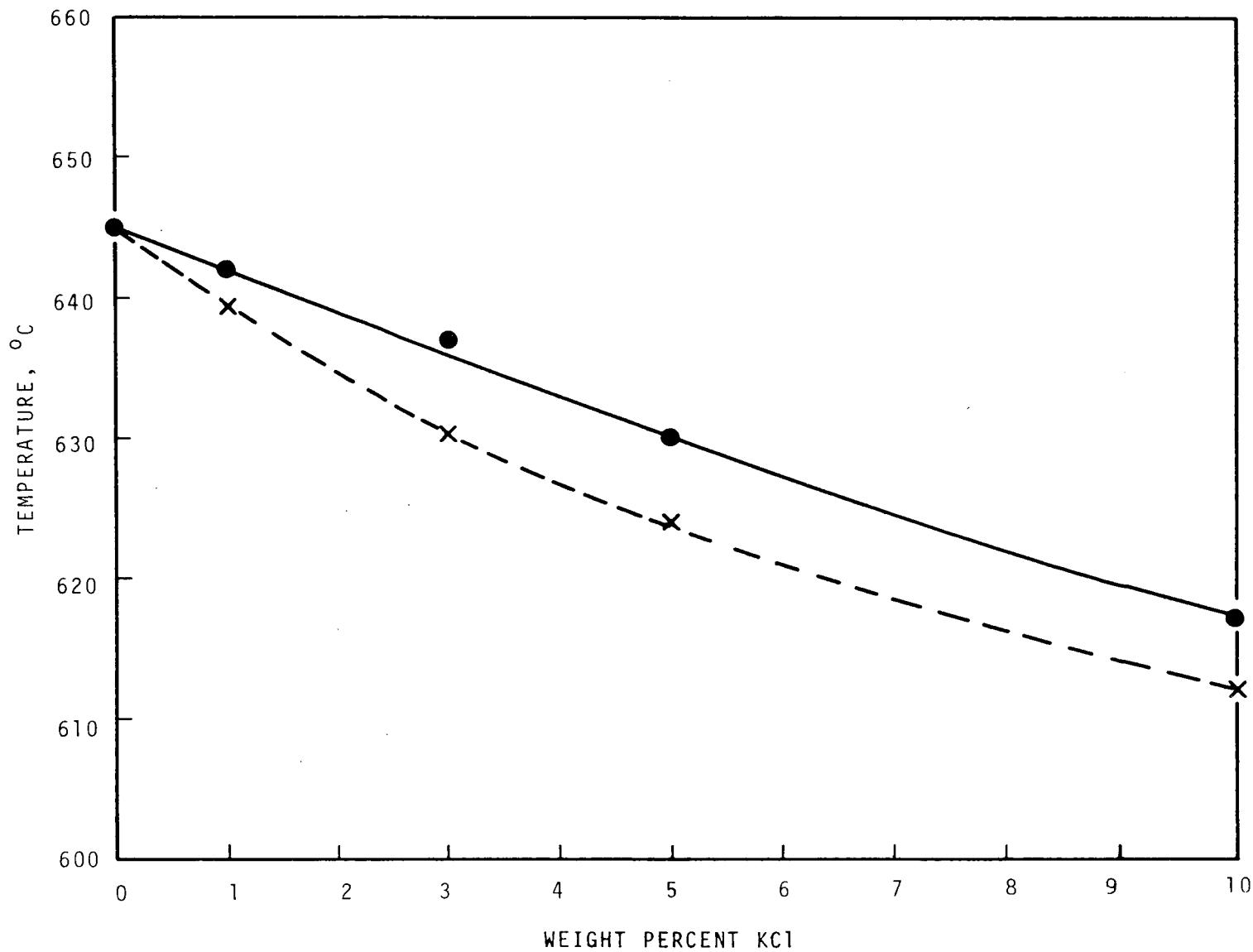


FIGURE 2 PHASE DIAGRAM FOR THE SYSTEM CsCl-KCl (0-10 wt% KC1)

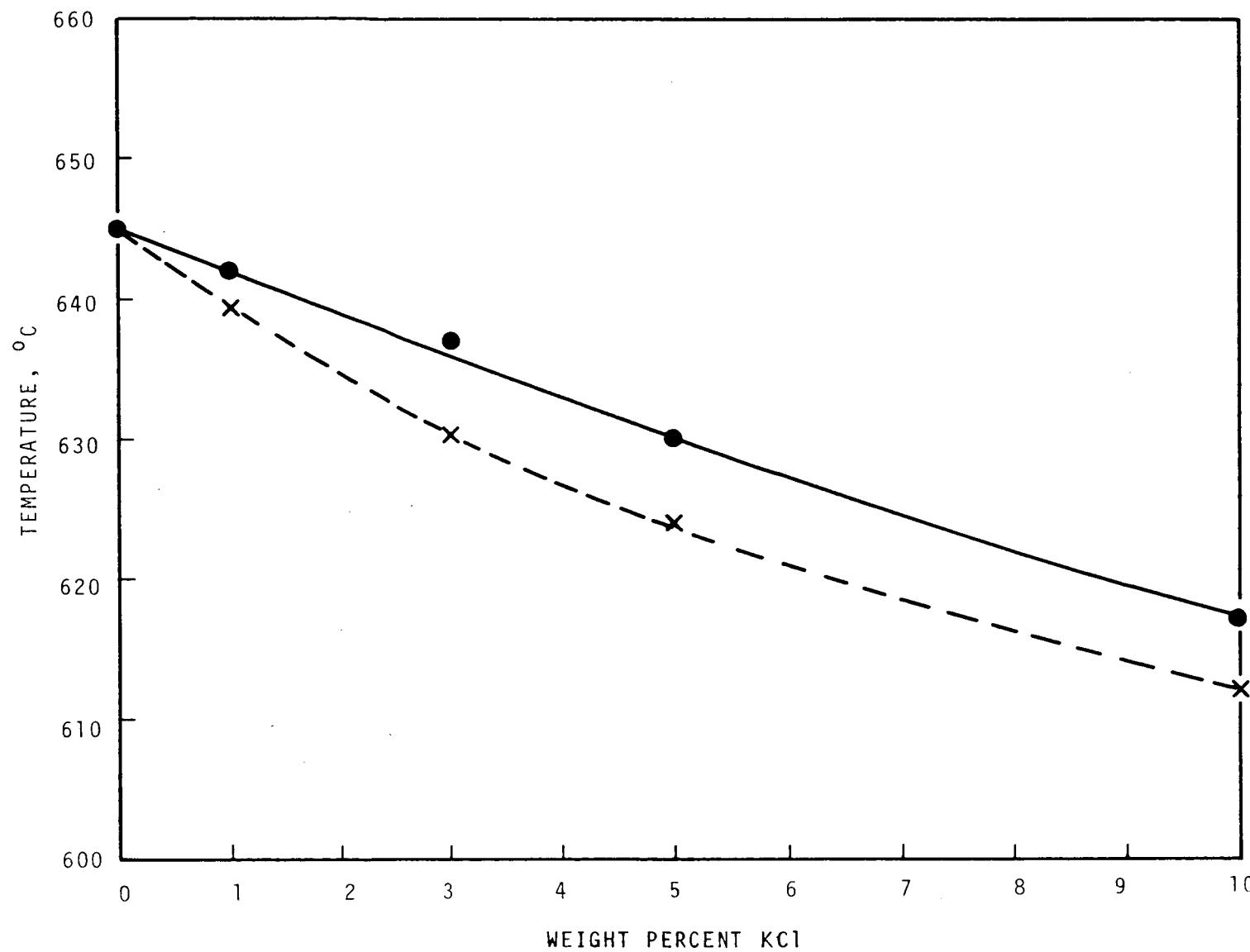


FIGURE 2 PHASE DIAGRAM FOR THE SYSTEM CsCl-KCl (0-10 wt% KCl)

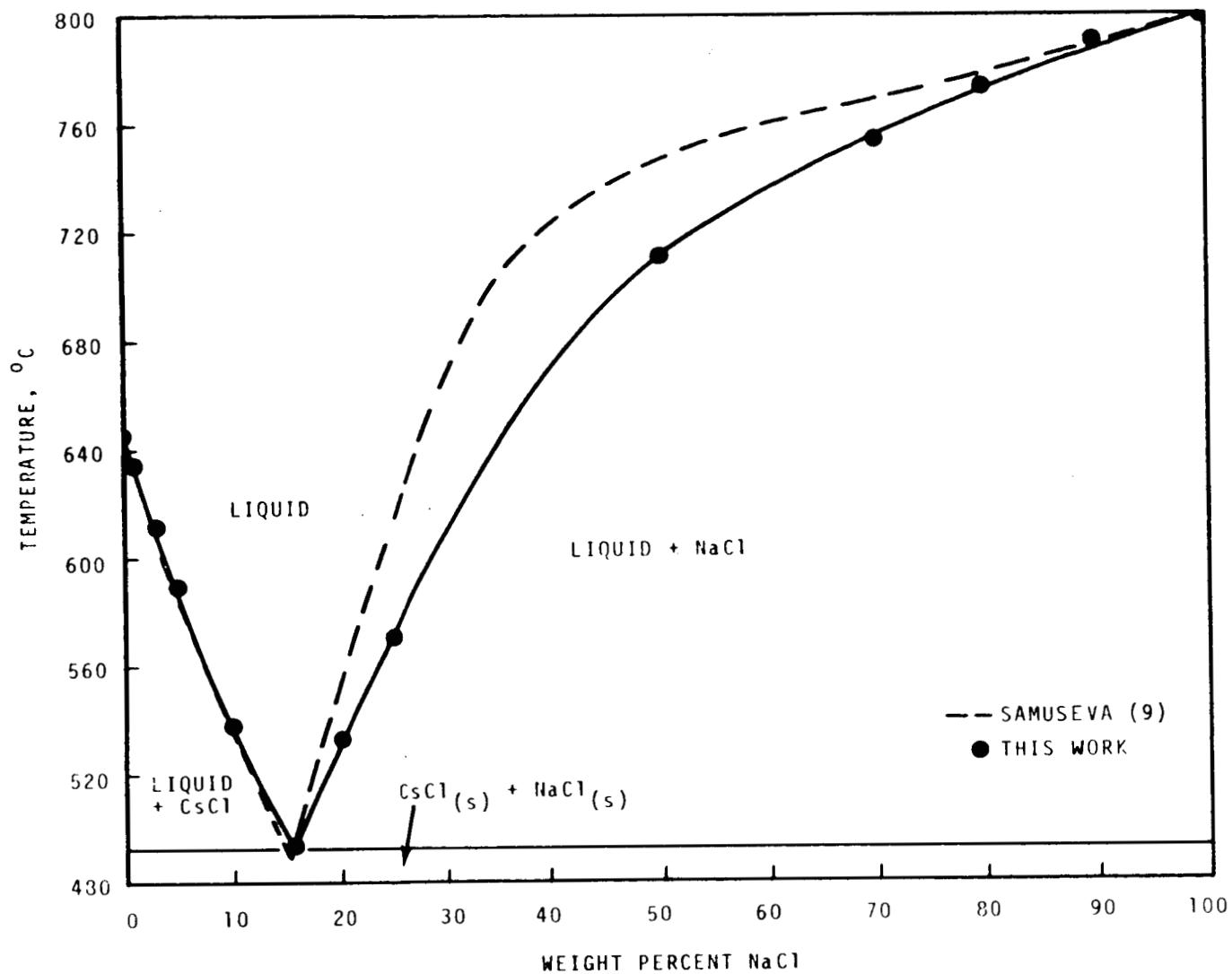


FIGURE 3 PHASE DIAGRAM FOR THE SYSTEM CsCl-NaCl

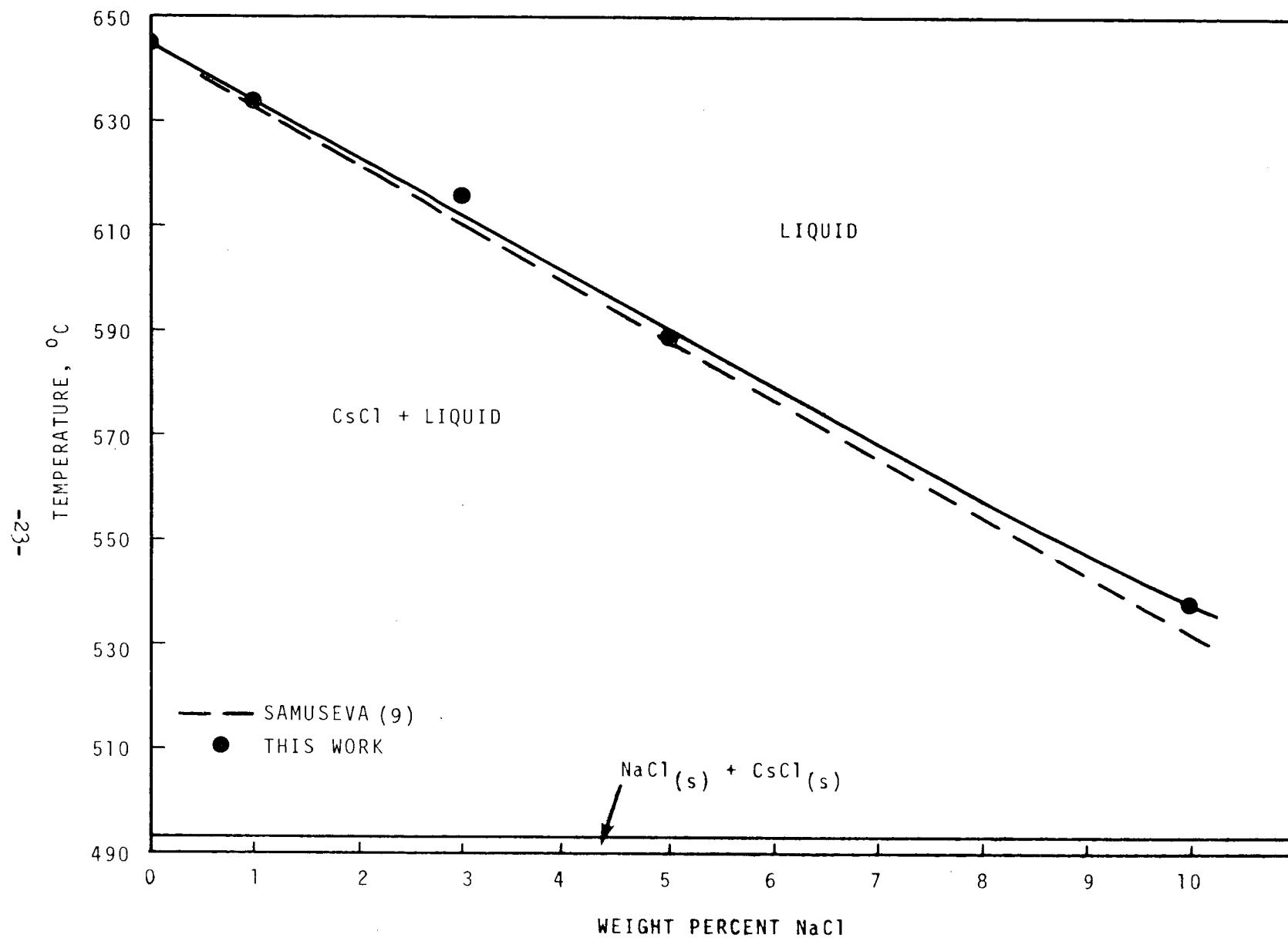


FIGURE 4 PHASE DIAGRAM FOR THE SYSTEM CsCl-NaCl (0-10 wt% NaCl)

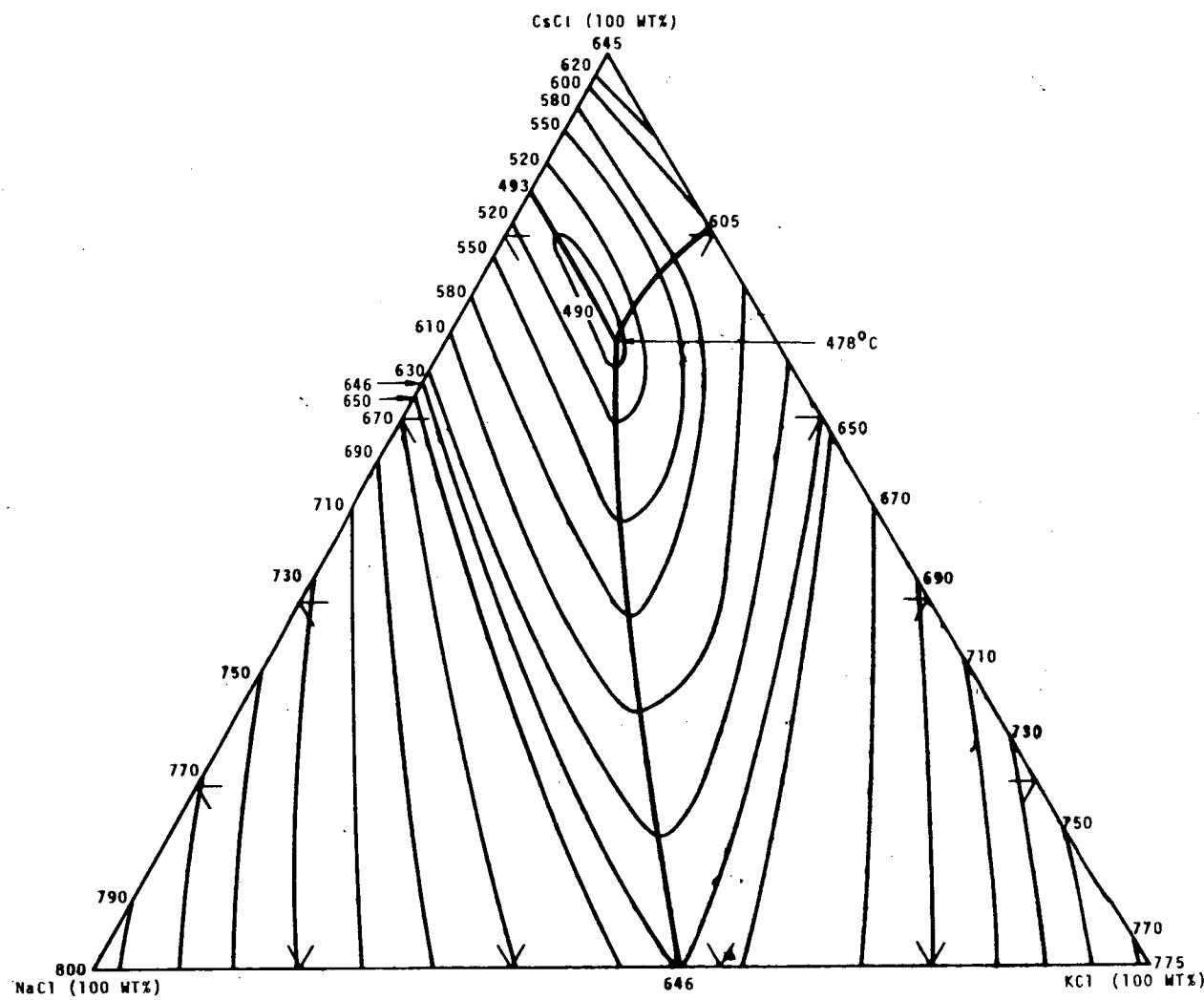


FIGURE 5 PHASE DIAGRAM FOR THE SYSTEM $\text{CsCl}-\text{KCl}-\text{NaCl}$ (Composition in wt%)

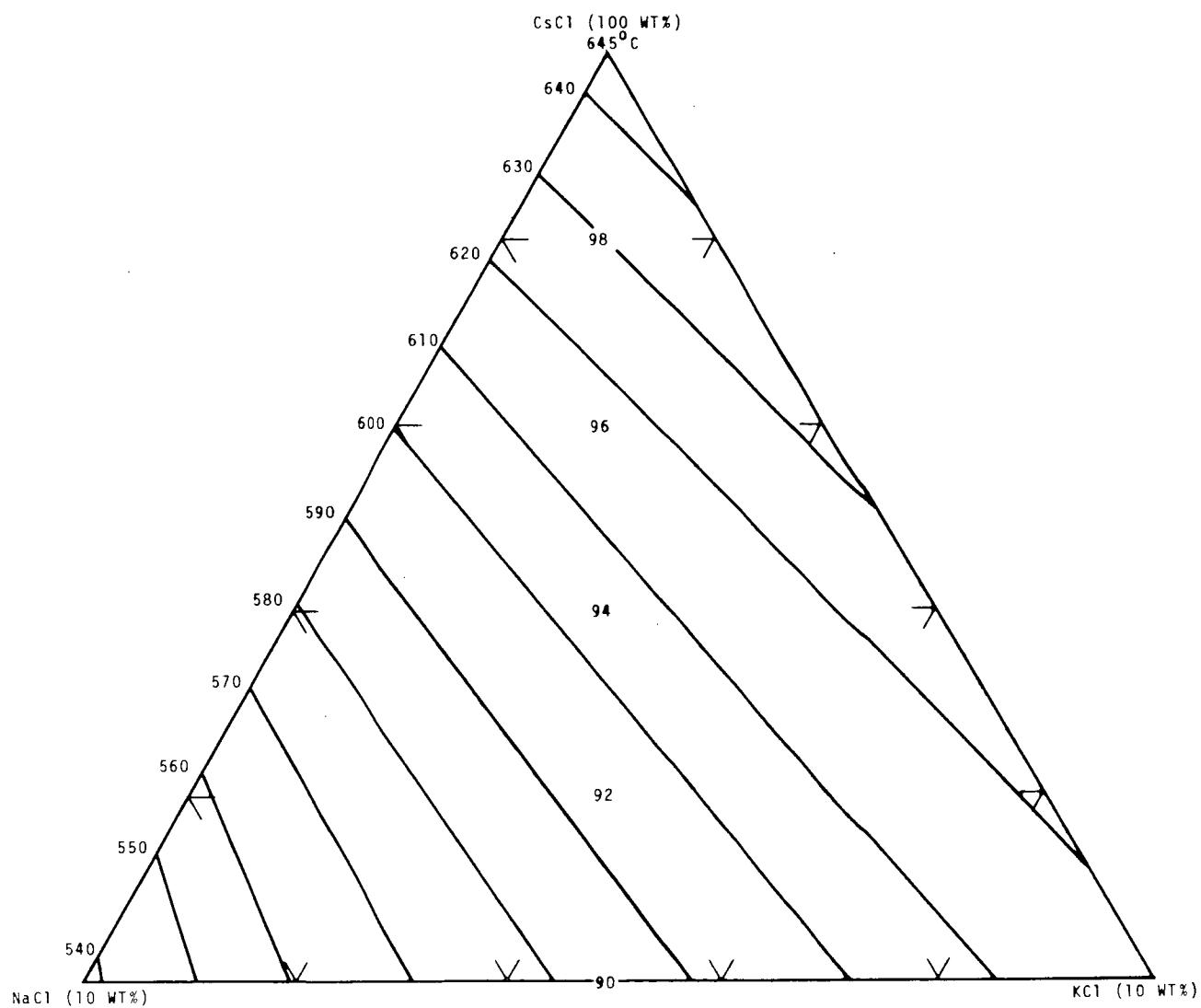


FIGURE 6 PHASE DIAGRAM FOR THE SYSTEM CsCl-KCl-NaCl (Composition in wt%)

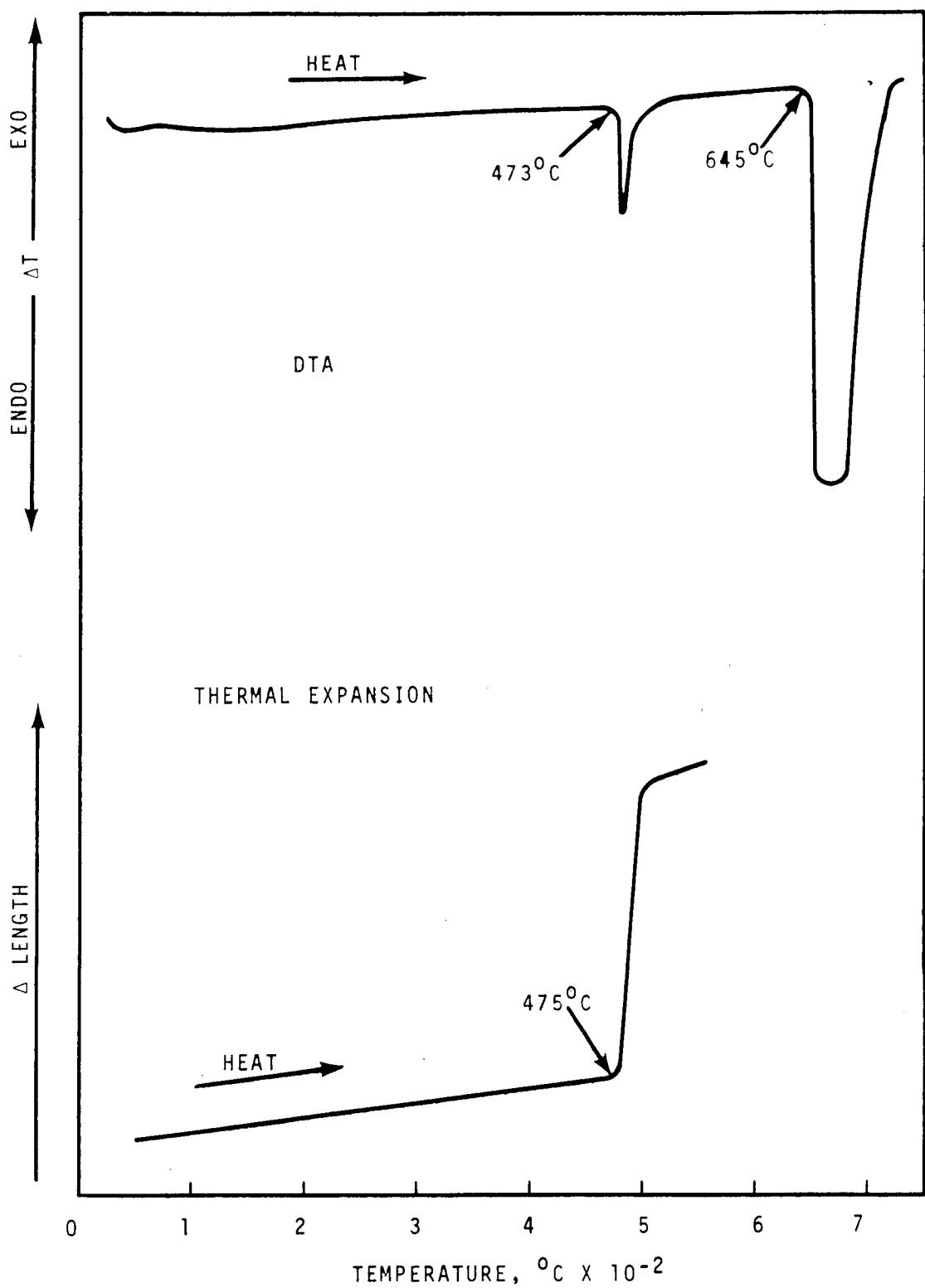


FIGURE 7 THERMAL EXPANSION AND DTA CURVES
FOR PURE CESIUM CHLORIDE ON HEATING

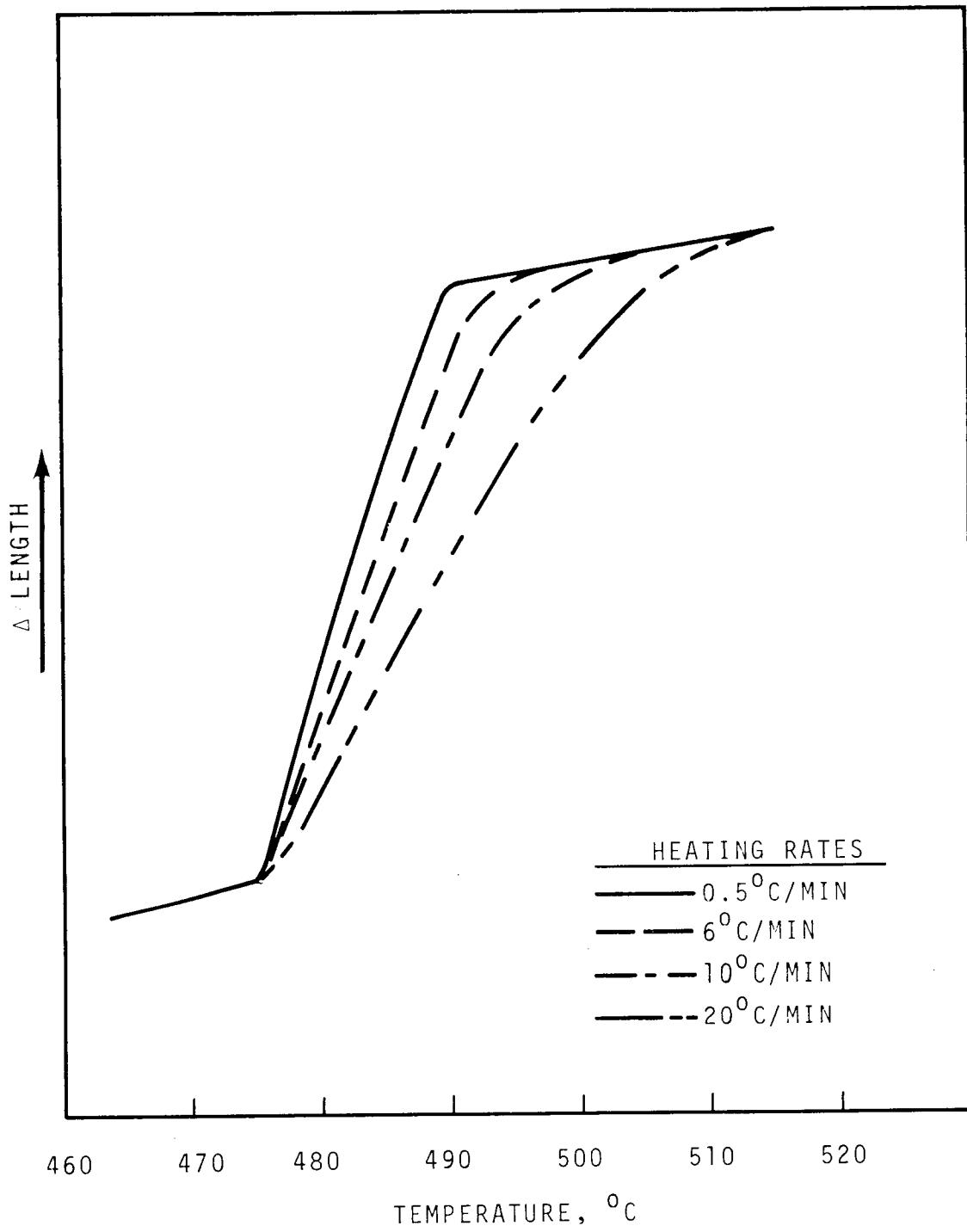


FIGURE 8 THE EFFECT OF HEATING RATE ON CsCl PHASE TRANSITION AS DETERMINED BY THERMAL EXPANSION MEASUREMENTS

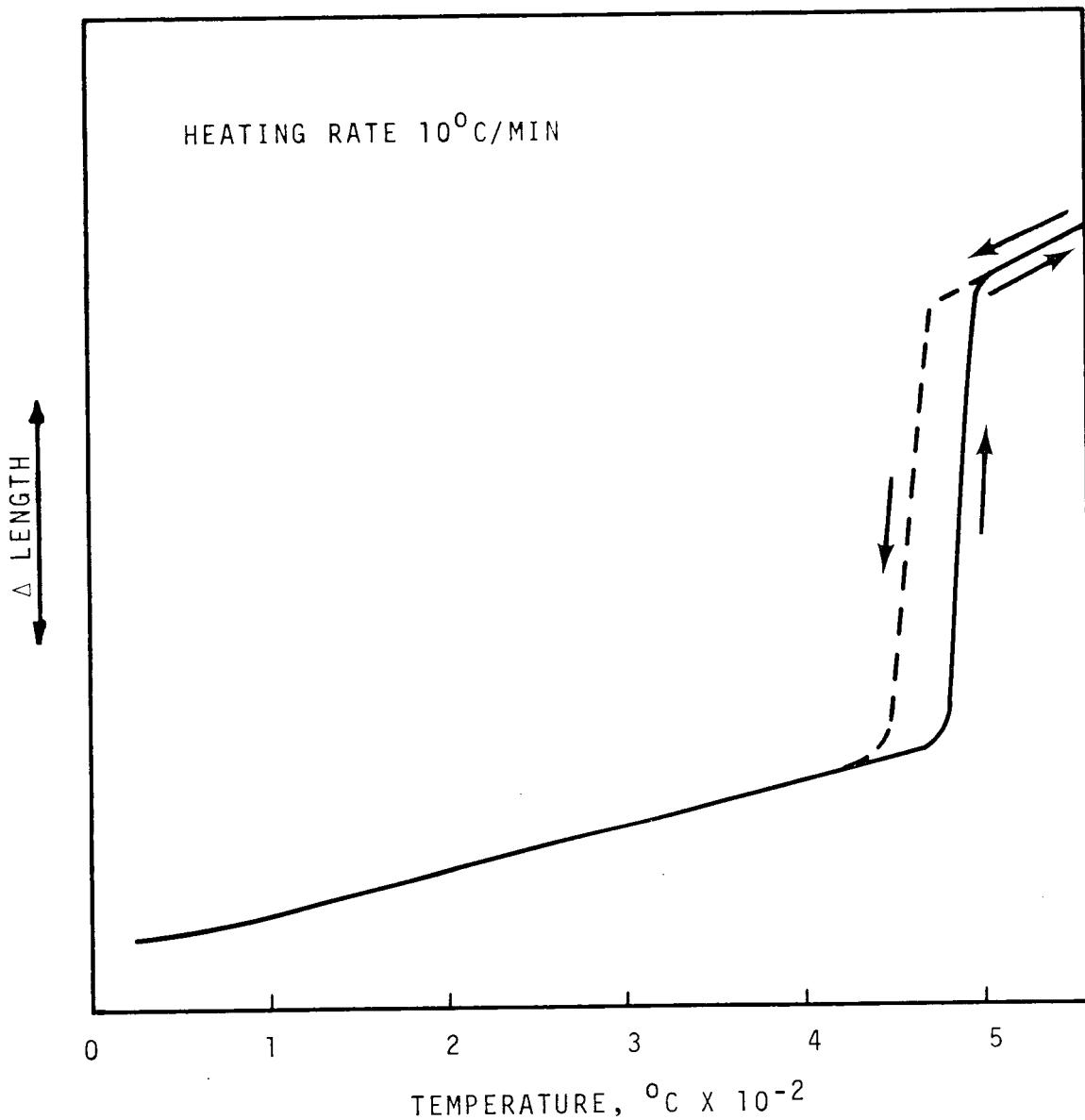


FIGURE 9 THERMAL EXPANSION AND CONTRACTION
OF CsCl ON HEATING AND COOLING

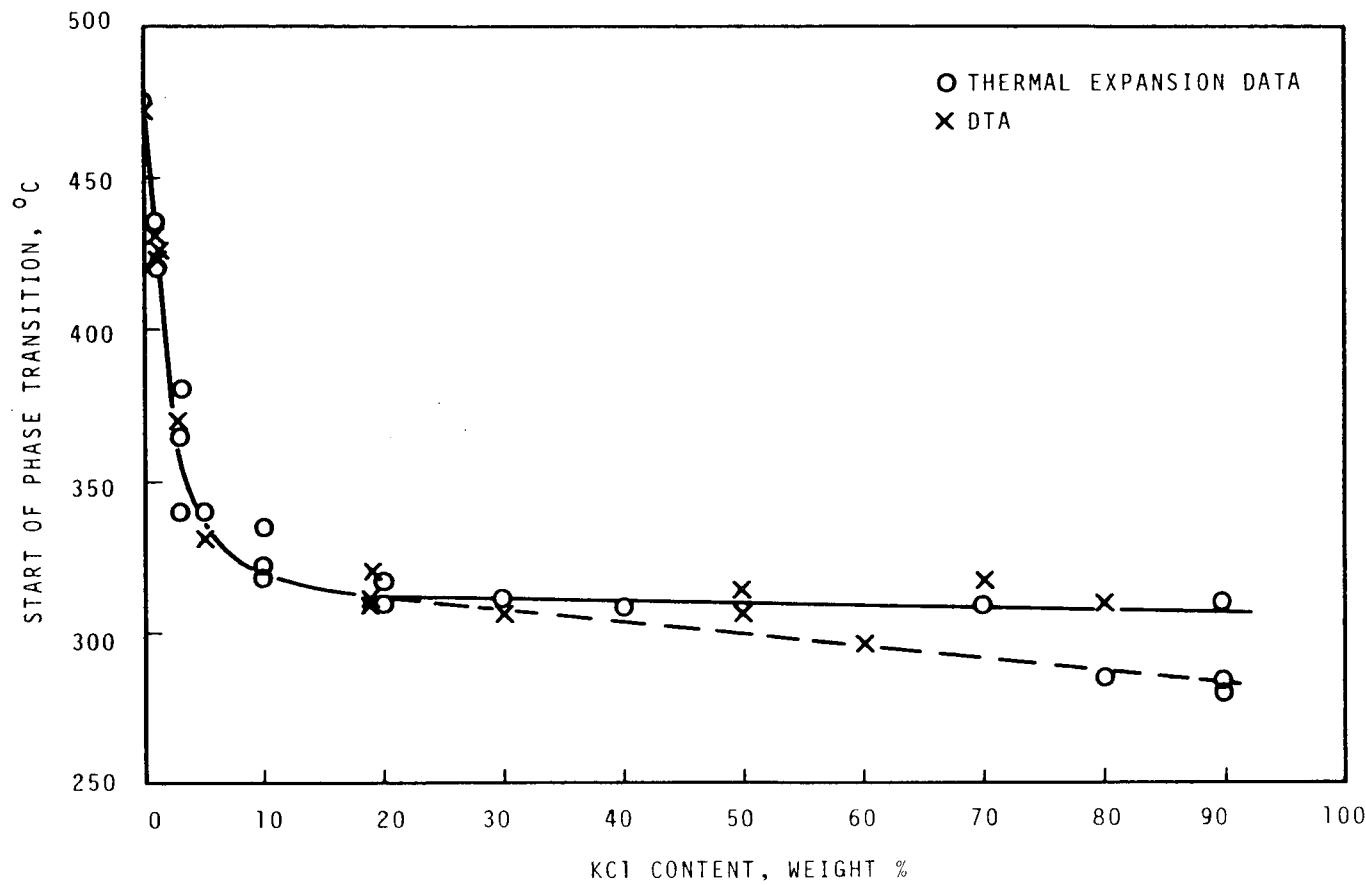


FIGURE 10 START OF PHASE TRANSITION FOR CsCl-KCl BINARY AS A FUNCTION OF KCl CONTENT

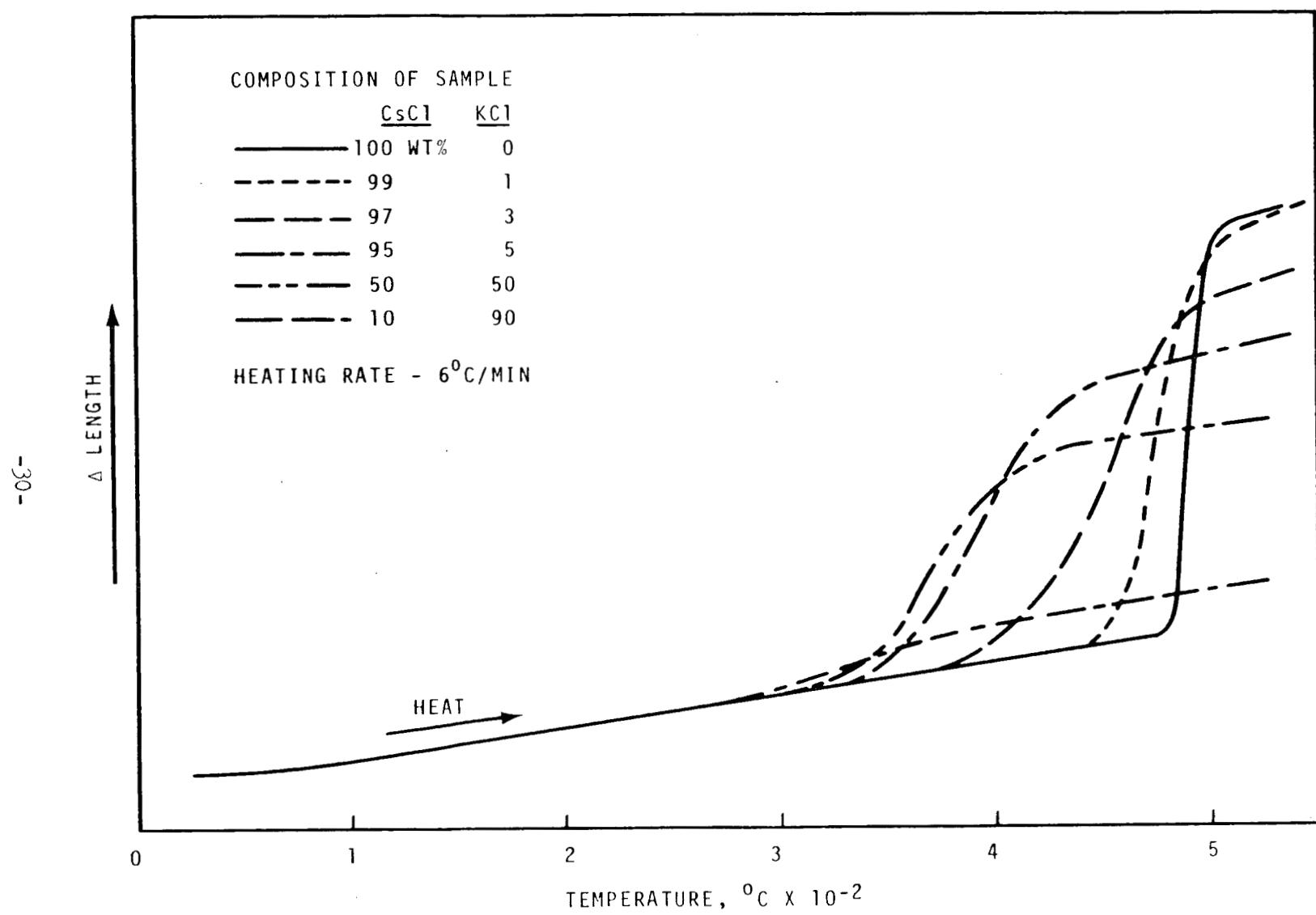


FIGURE 11 THE EFFECT OF KCl CONTENT ON THE RATE OF PHASE TRANSITION

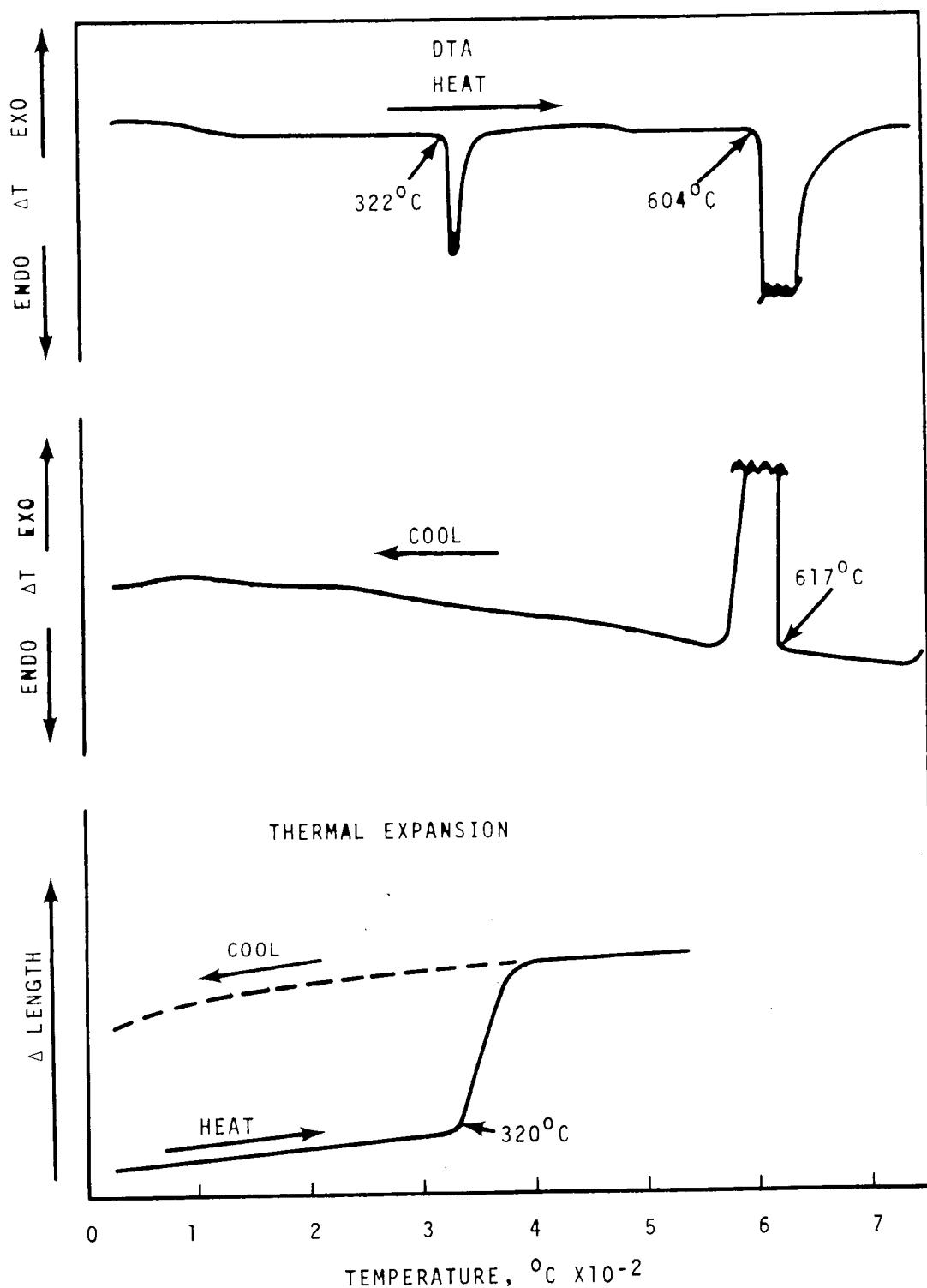


FIGURE 12 DTA AND THERMAL EXPANSION MEASUREMENTS
FOR ANNEALED CsCl-10 wt% KCl SAMPLES

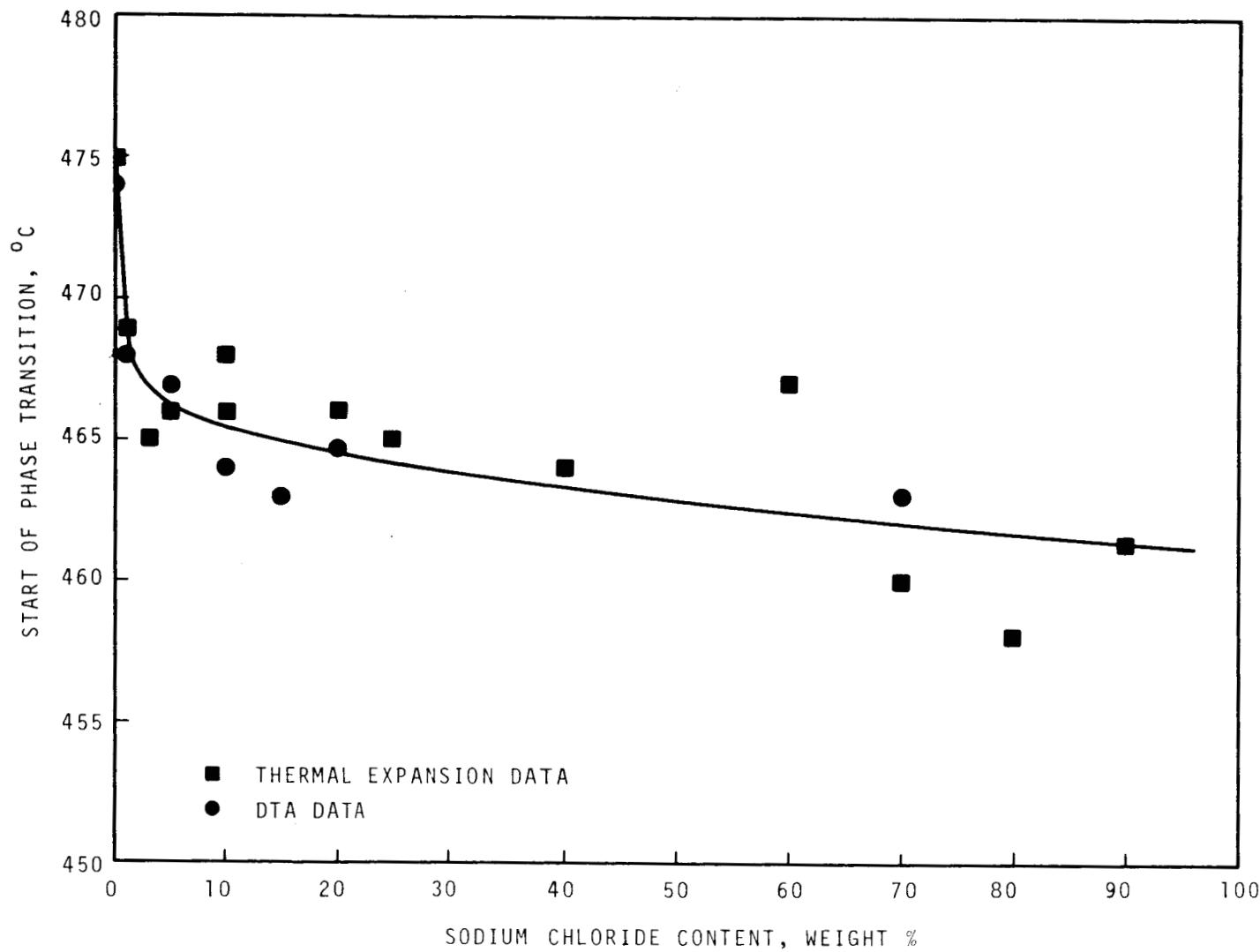


FIGURE 13 THE EFFECT OF NaCl CONTENT ON THE PHASE TRANSITION TEMPERATURE OF THE CsCl-NaCl SYSTEM

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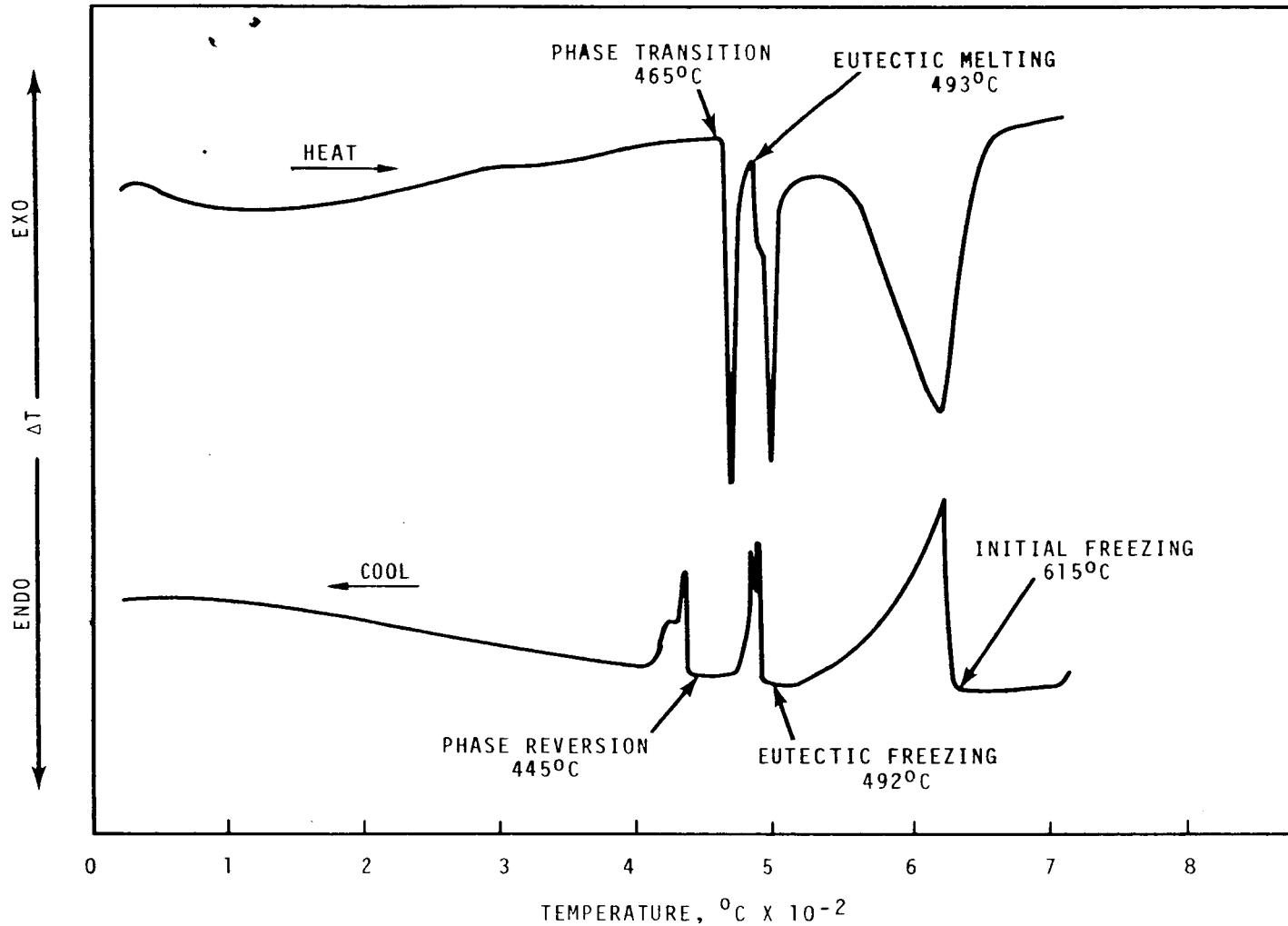


FIGURE 14 DIFFERENTIAL THERMAL ANALYSIS OF A CsCl-3 wt% NaCl SAMPLE

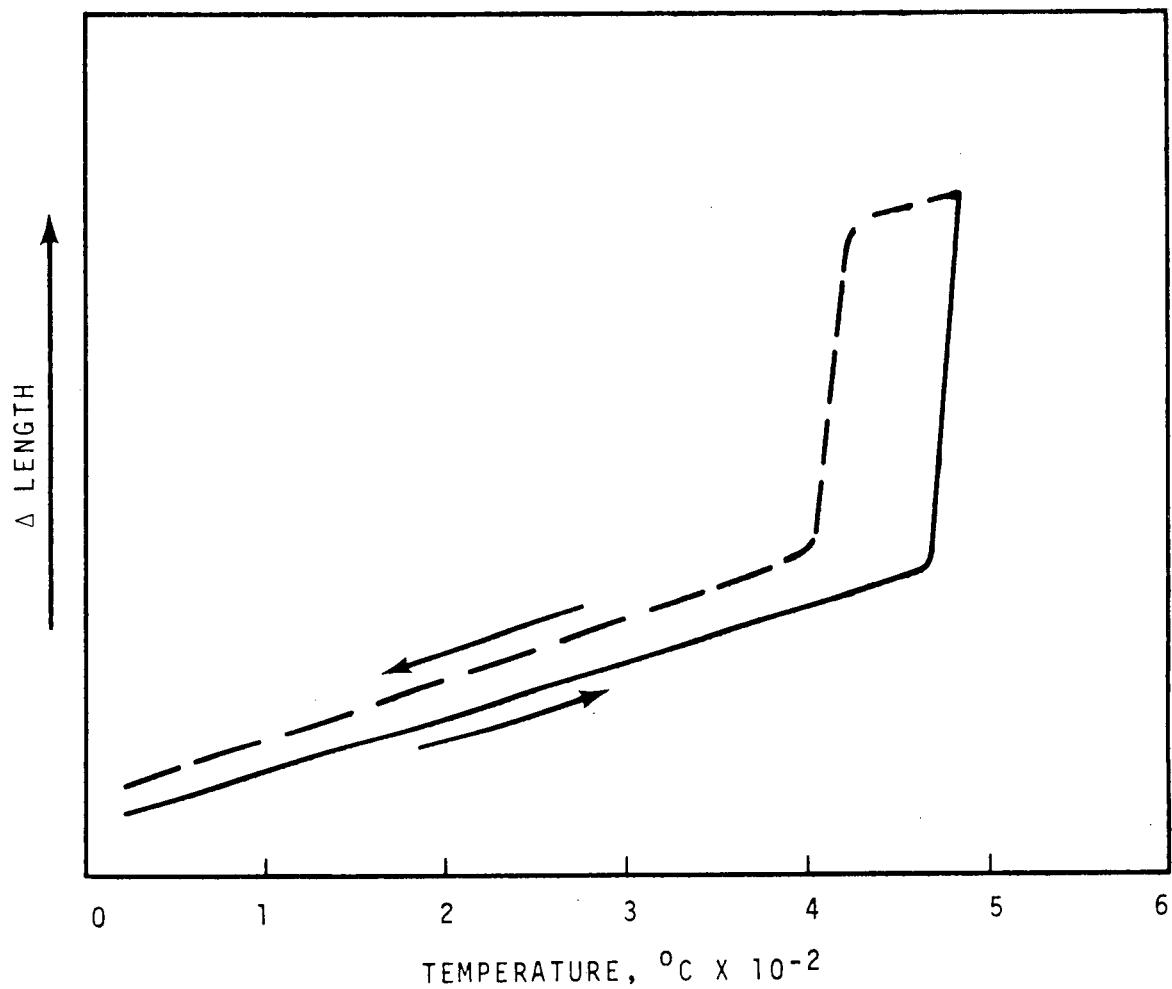


FIGURE 15 THERMAL EXPANSION OF A CsCl-10 wt% NaCl SAMPLE

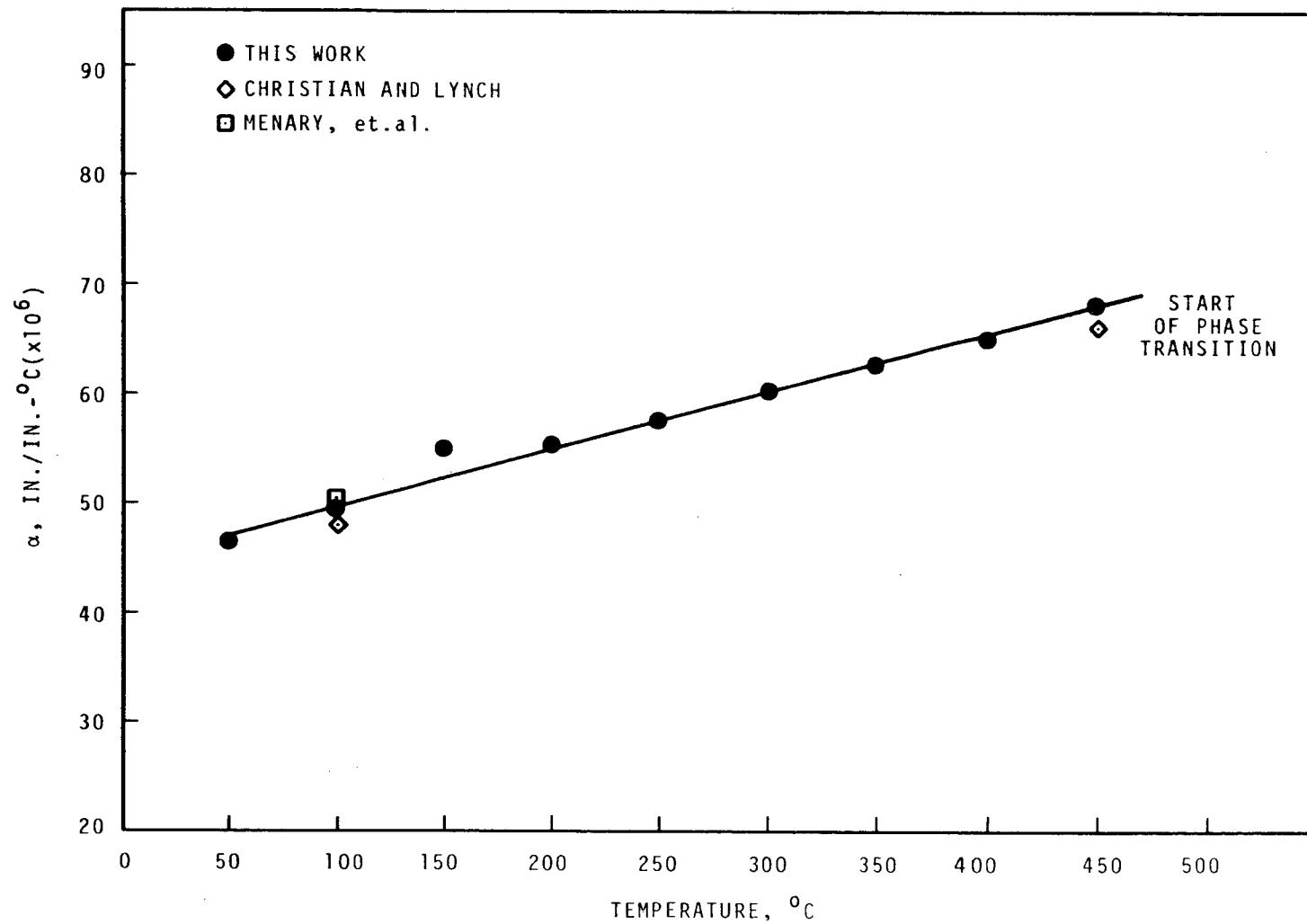


FIGURE 16 THERMAL EXPANSION COEFFICIENT FOR CsCl AS A FUNCTION OF TEMPERATURE

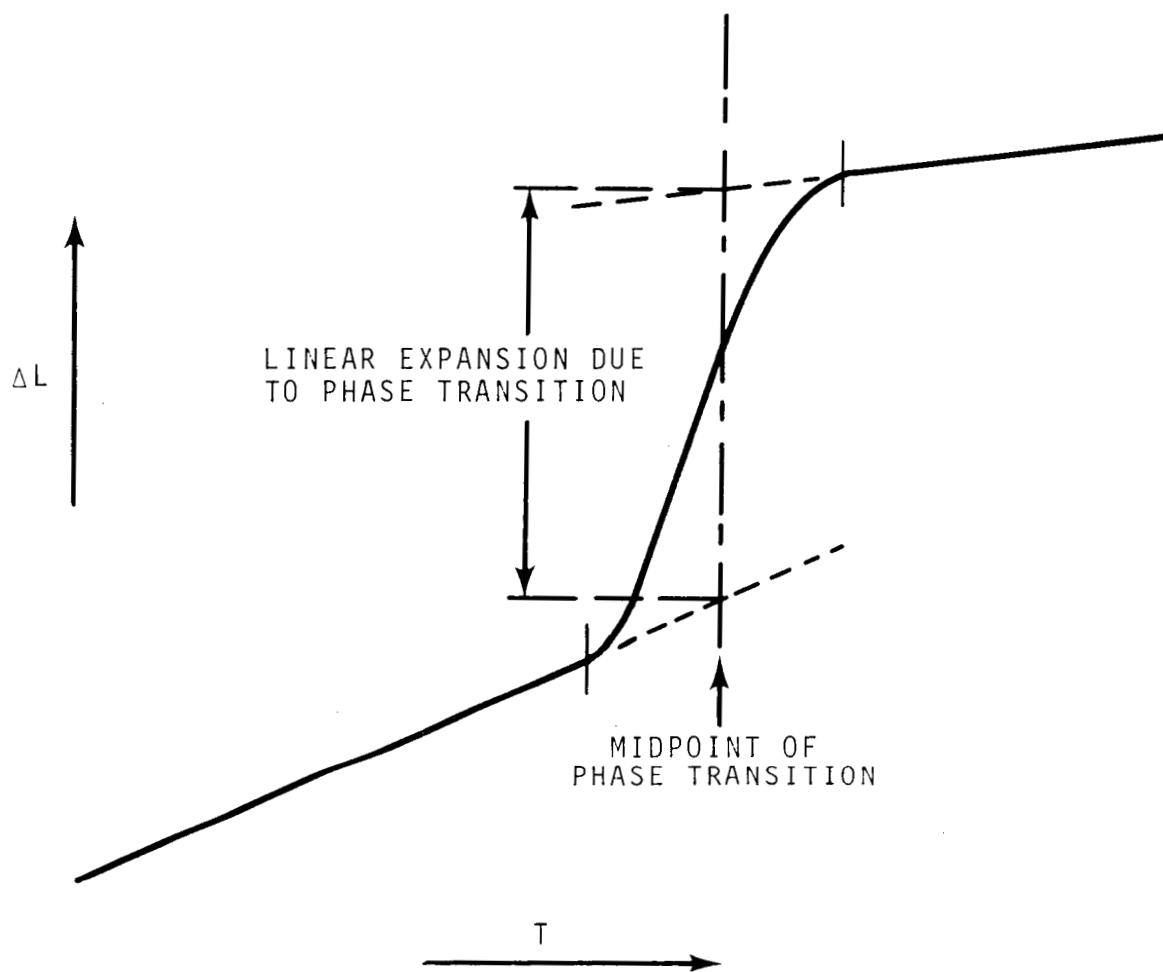


FIGURE 17 DETERMINATION OF LINEAR EXPANSION AT THE PHASE TRANSITION

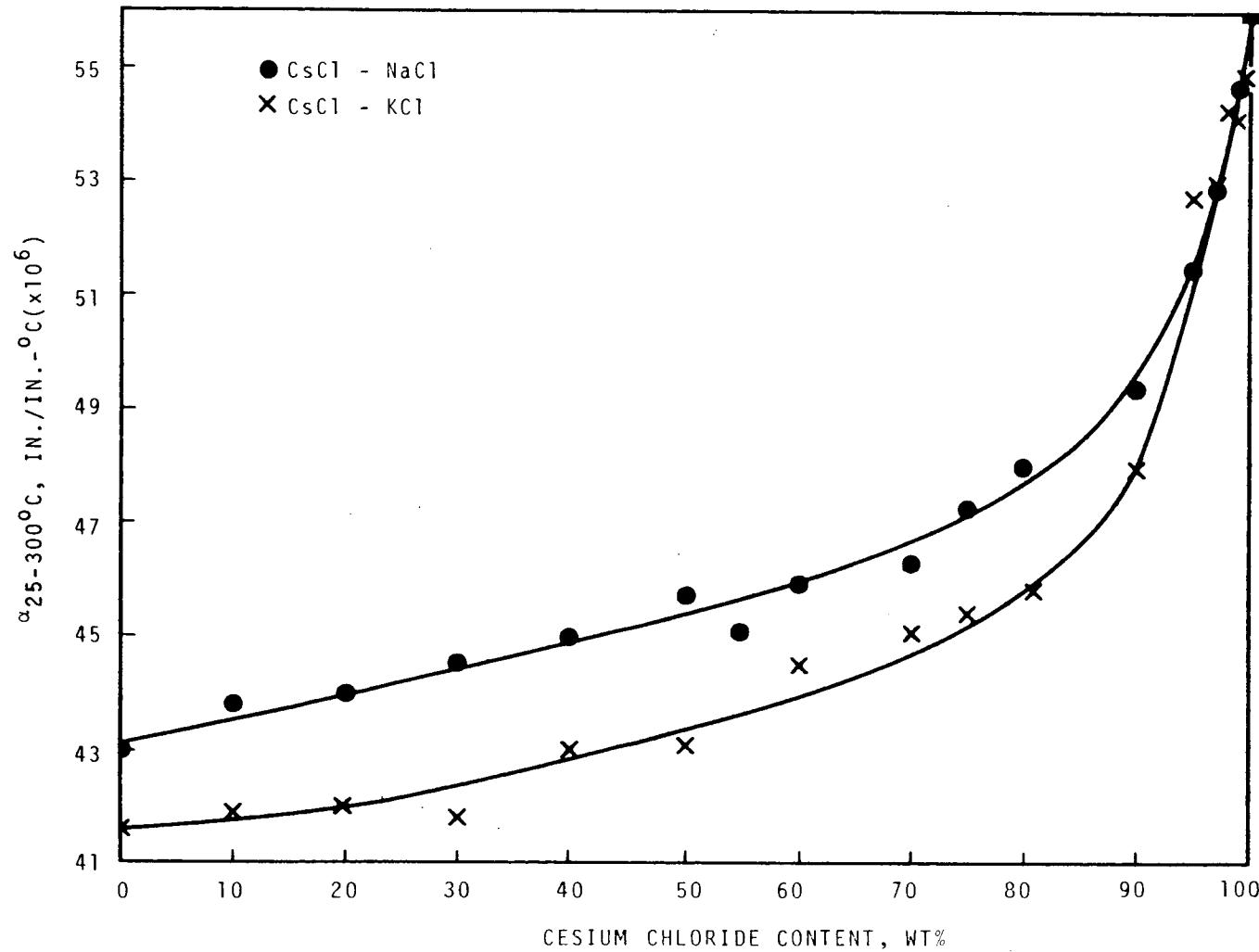


FIGURE 18 THE EFFECT OF COMPOSITION ON THE AVERAGE THERMAL EXPANSION COEFFICIENT BETWEEN 25-300°C FOR THE SYSTEMS CsCl-KCl AND CsCl-NaCl

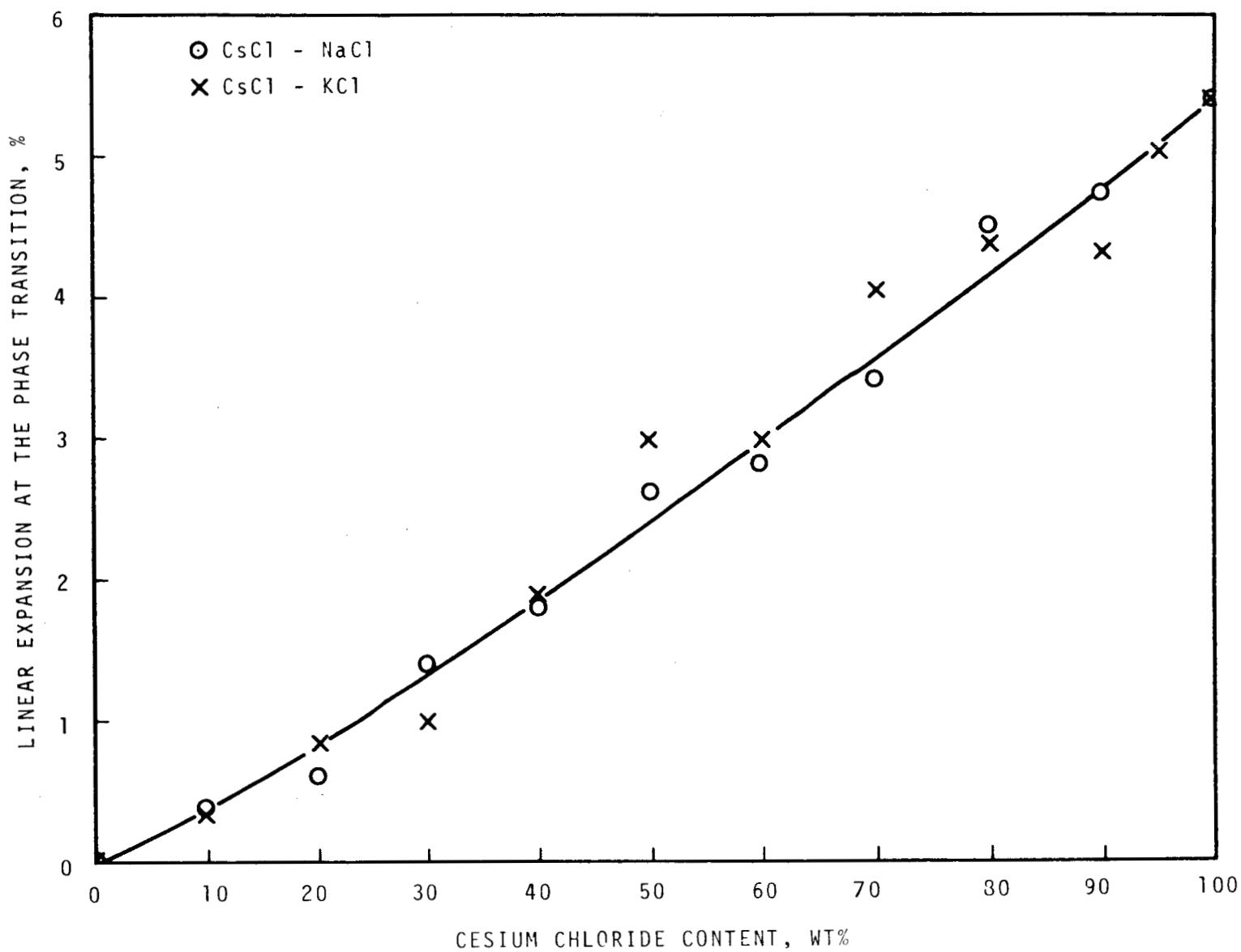


FIGURE 19. CHANGE IN LINEAR EXPANSION AT THE PHASE TRANSITION
WITH CsCl CONTENT FOR THE SYSTEMS CsCl-KCl and CsCl-NaCl

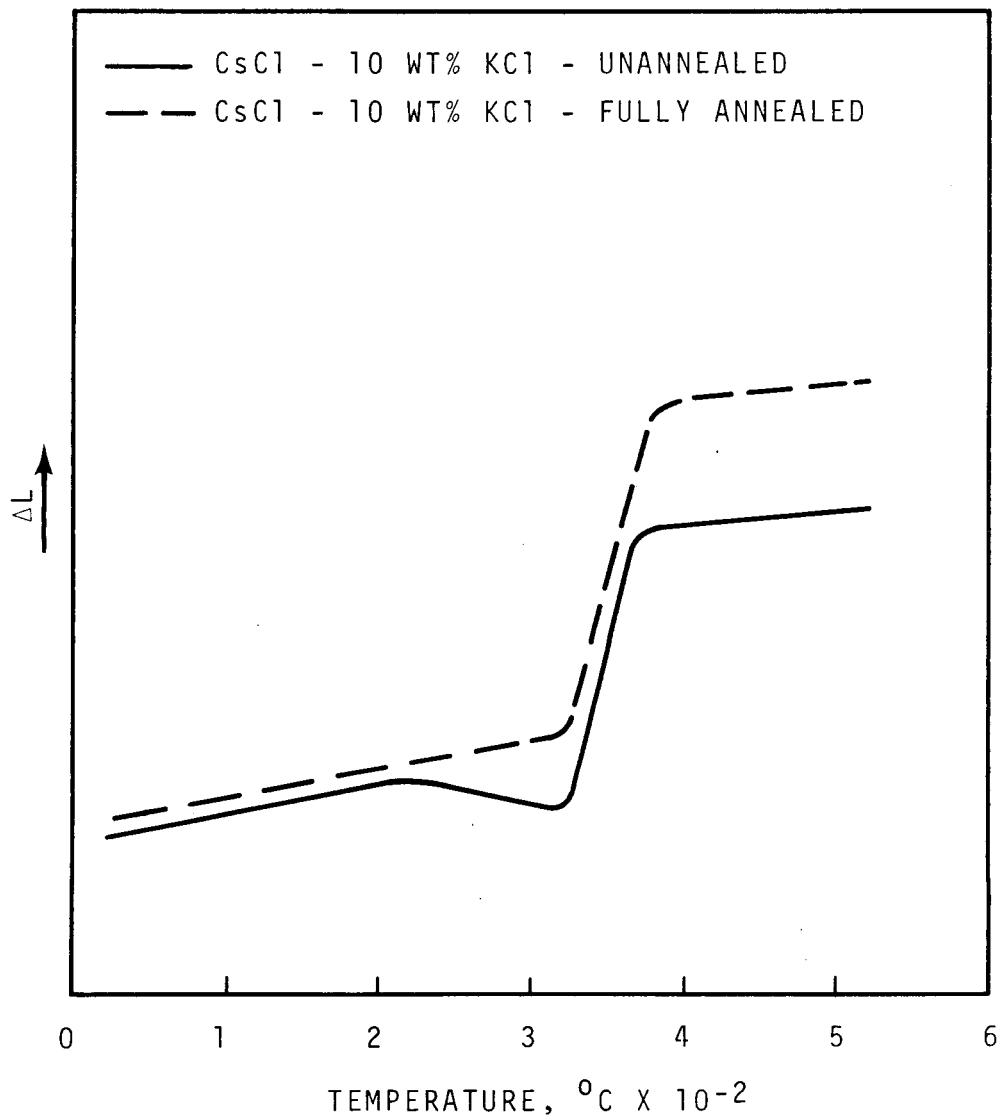


FIGURE 20 THERMAL EXPANSION CURVES
FOR ANNEALED AND UNANNEALED CsCl-10 wt% KCl SAMPLES

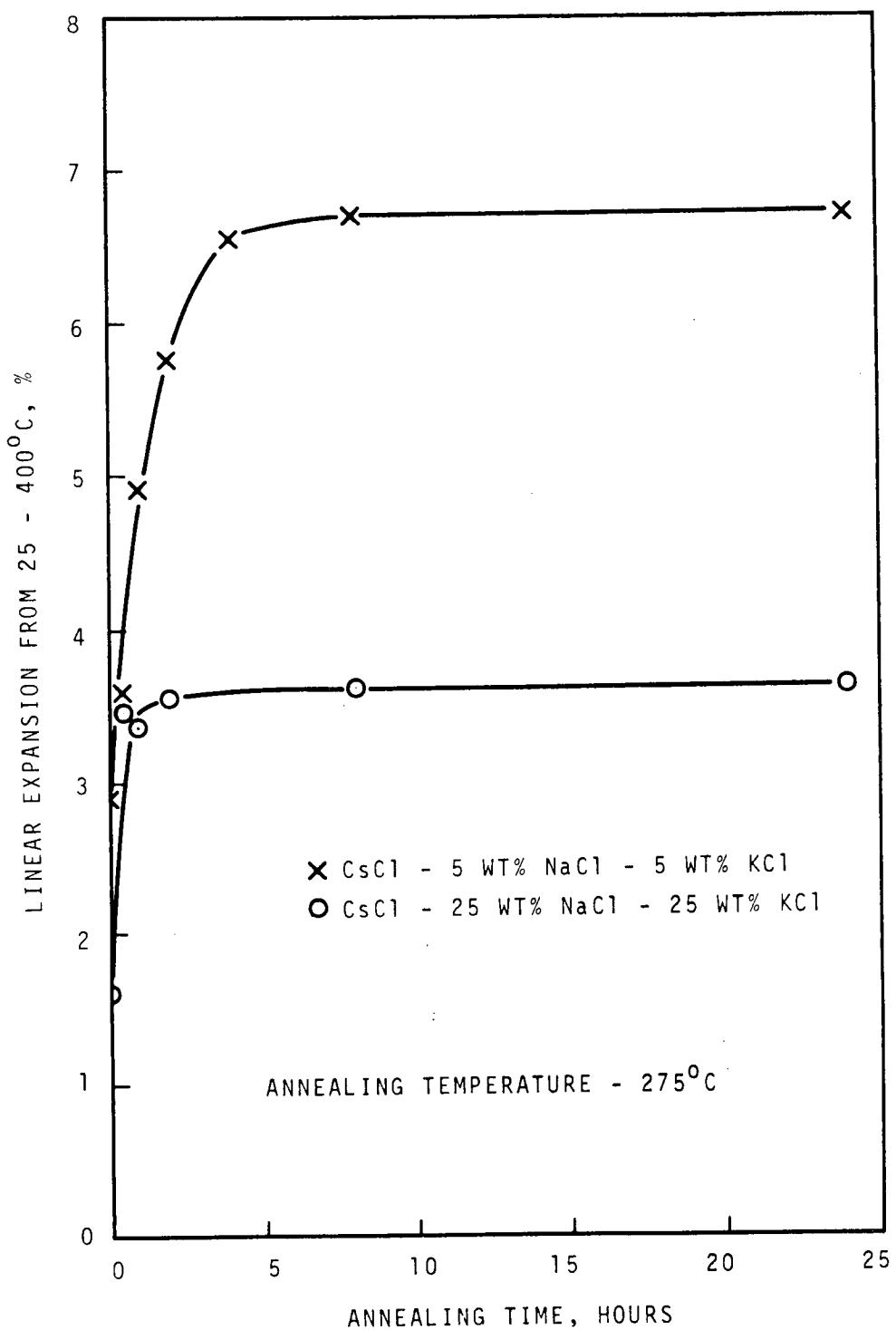


FIGURE 21 THE EFFECT OF ANNEALING TIME
ON THE LINEAR EXPANSION OF CsCl-NaCl-KCl SAMPLES

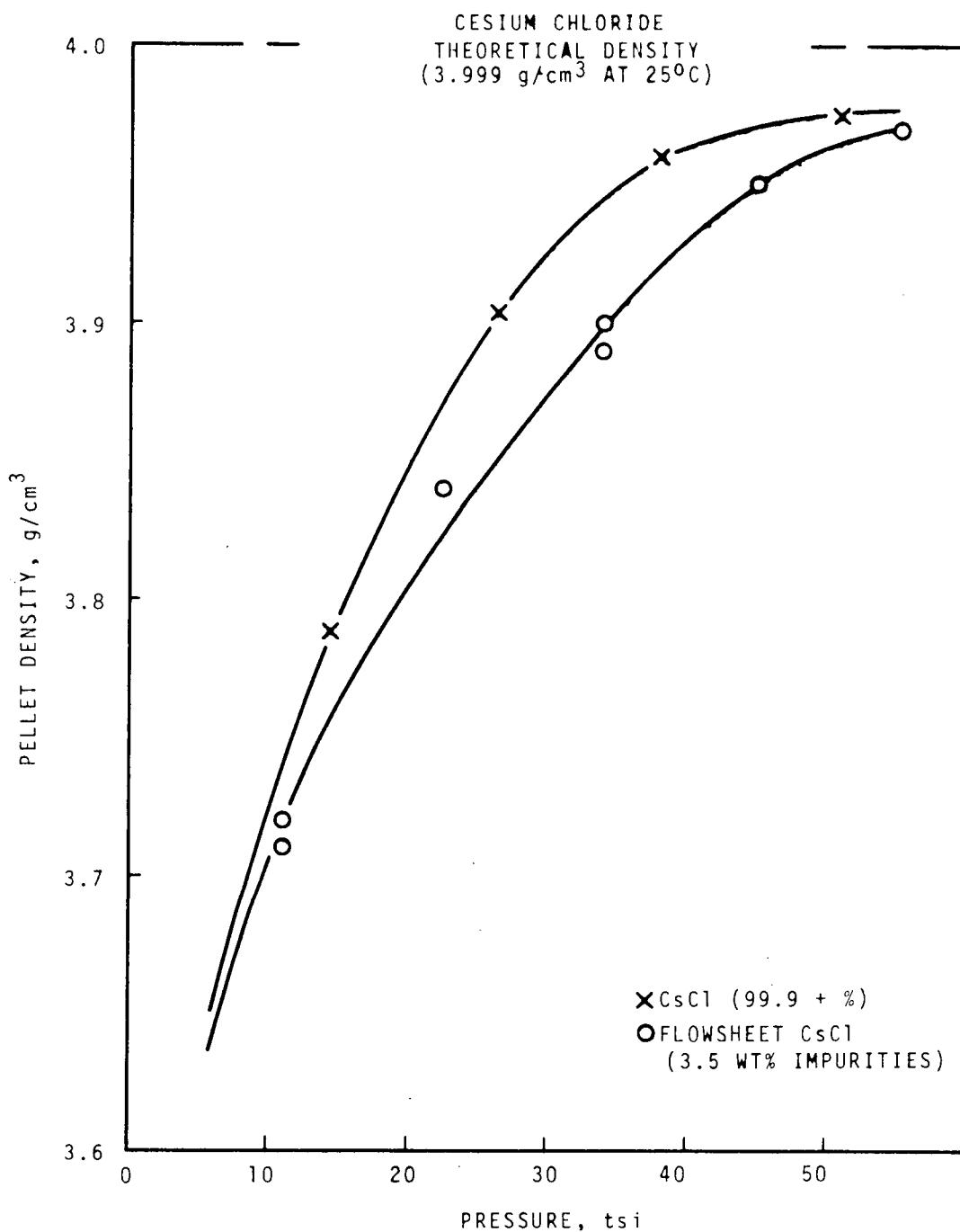


FIGURE 22 COMPACTION OF CsCl BY COLD PRESSING

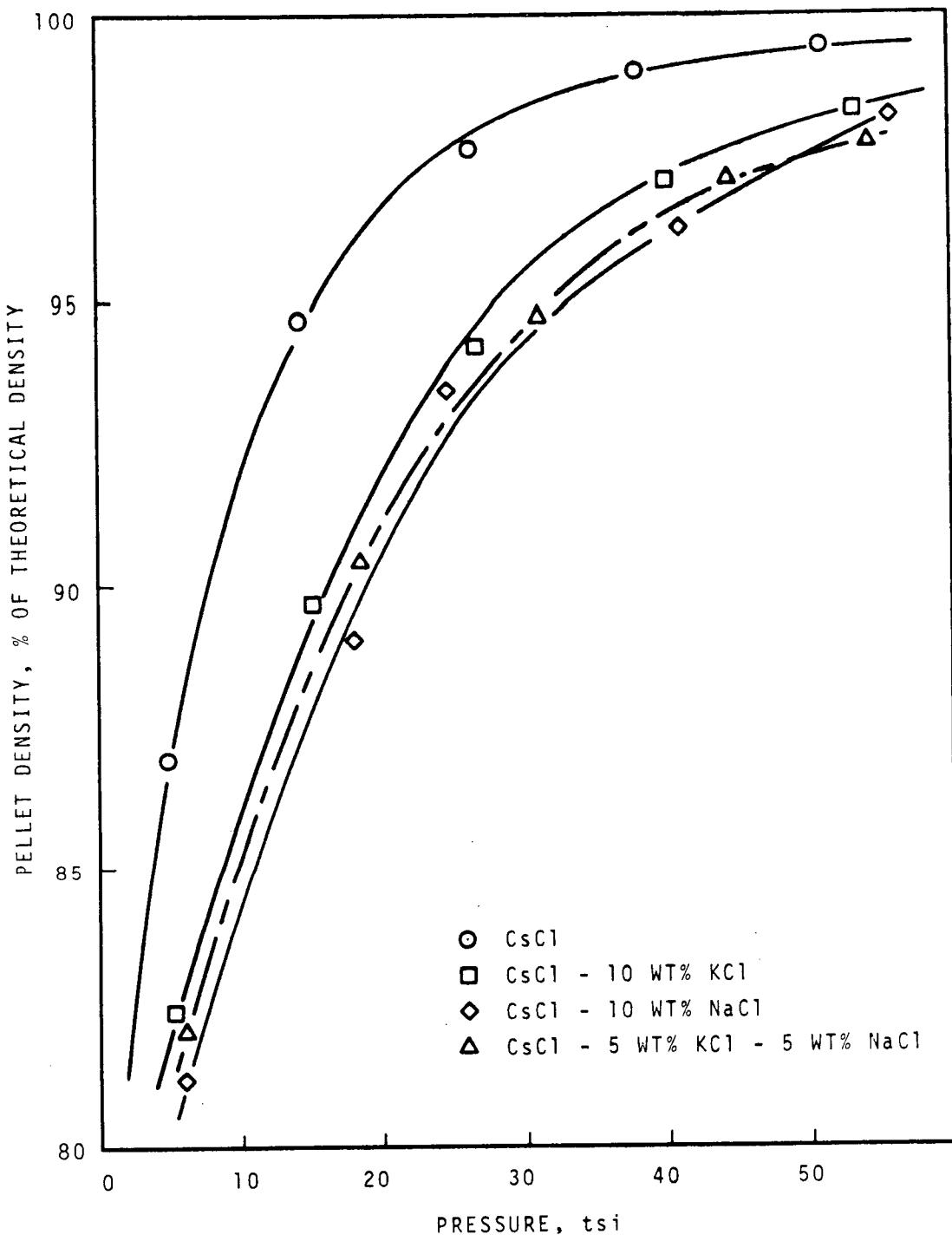


FIGURE 23 COLD PRESSING OF ALKALI CHLORIDE MIXTURES

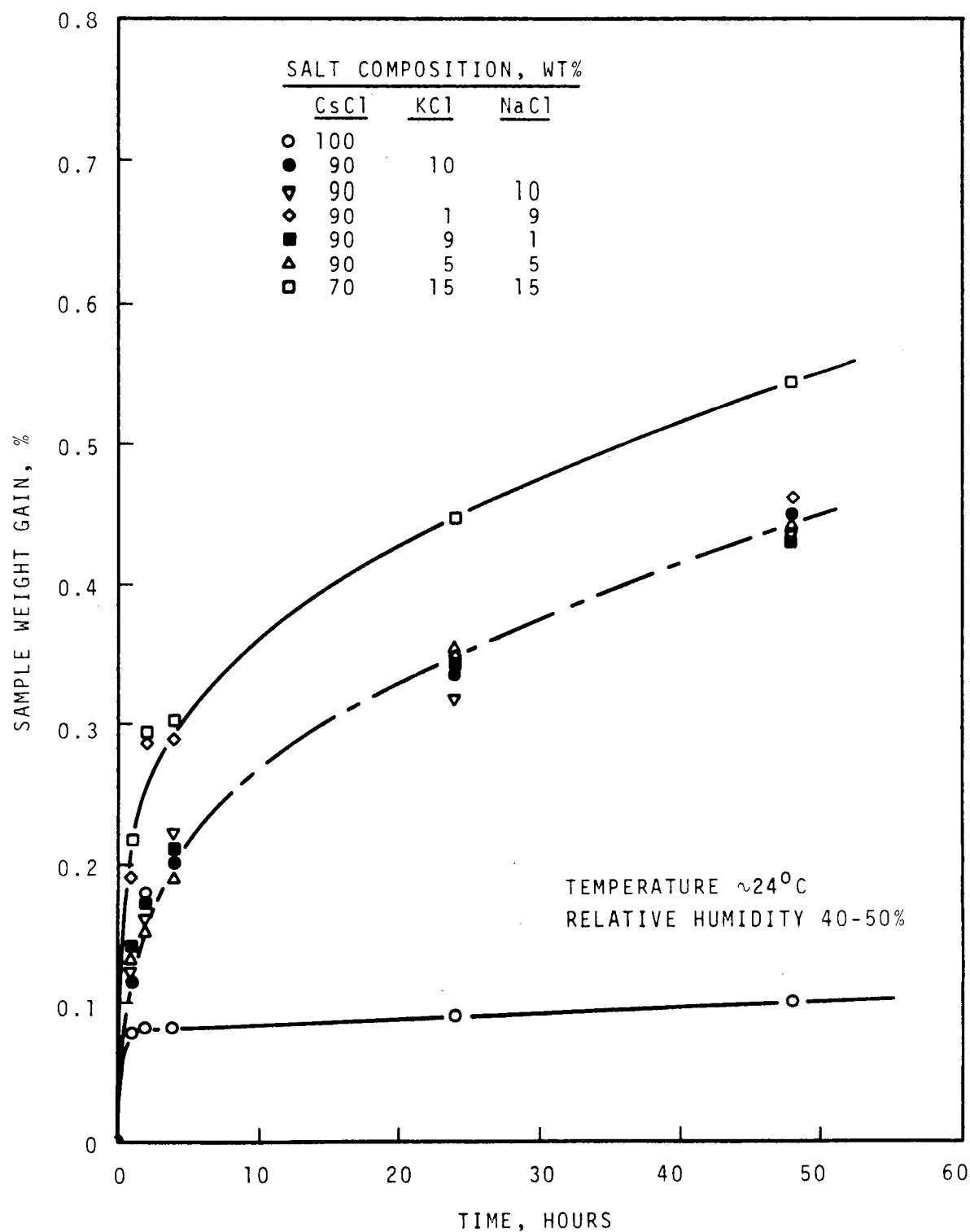


FIGURE 24 ADSORPTION OF WATER BY CsCl AND ALKALI CHLORIDE MIXTURES