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Thermoanlytical Investigation of Latent Heat Thermal Energy Storage Materials

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ABSTRACT

For solar energy utilization, waste heat recovery and load levelling, latent thermal energy storage is a useful tool, and the thermophysical properties, such as latent heat and specific heat capacity, of the materials are very important as well as thermal stability. DSC and TG have been applied for the purpose to the materials, such as polyethylene, urea, pentaerythritol and eutectic mixtures of alkaline hydroxides with alkaline nitrates or nitrites. Performance of polyethylene latent thermal energy storage equipment is also described.

INTRODUCTION

Among thermal energy stroage methods, i.e., utilization of sensible heat, latent heat and reversible chemical reactions including dilution of concentrated aqueous solutions and adsorption, latent heat thermal energy storage has some advantages over the others. For instance, it can store heat in relatively high density and release heat at almost constant temperature, and the released heat can be used effectively, so that it is of high quality. Thus, latent heat thermal energy storage is applicable to solar thermal energy utilization and waste heat recovery. It is also one of useful potential candidates for adjusting electric power generation from large capacity power plants, such as nuclear power plants, to daily variation of electric comsumption.

On the other hand, the latent heat thermal energy storage depends on the materials which undergo fusion or crystalline transition at a desired temperature (a desired working temperature of the equipment) with large latent heat. In research and development of the technology, thermophysical properties, such as heat of fusion or transition and specific heat capacity, are very important. The present author and his coworkers first preliminarily screened the candidate materials from the latent heat and the material cost by using thermodynamic data compilations. Then, thermoanalytical methods, such as DSC and TG, have been applied to evaluate the selected materials, including polyethylene, urea, pentaerythritol,

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and eutectic mixtures of alkaline hydroxides with alkaline nitrate or nitrite. These thermoanalytical methods are very useful for the evaluations of thermophysical properties, thermal stability and melting-and-crystallizing behavior, such as supercooling. In this report these results are described together with performance of a polyethylene latent thermal storage equipment.

RESULTS AND DISCUSSION

MATERIALS SCREENING

Some characteristics of the materials have large influence on the performance of latent thermal storage equipments. For the screening of the materials, relations between the characteristics of the materials and the performance of the equipment are first considered.[1,2,3) Although the performances are not directly related to the characteristics because design of the heat exchanger and materials of the container for the storage materials have also effects on the performance, certain characteristics of the storage materials have definite influence on the performance. For instance, the temperature of fusion or transition decides the working temperature of the equipment, and the energy density of the equipment can not be over the limit of the latent heat. The behavior of fusion, transition and crystallization has also definite effect on the power density, the response to load and the exergy efficiency. The manufacturing cost of the equipment is deeply dependent on the price of the storage materials and the compatibility of the storage materials with the container, which also limits the life together with the thermal stability of the materials. Toxicity and reactivity, such as explosion and ignition, are also very important characteristics to be considered from the viewpoint of the system safety. These characteristics mentioned above should first be taken into accounts in the screening. Among them, the temperature of fusion and transition and the latent heat are available readily from thermodynamic data compilations,[4,5) and the price of the storage materials can also be easily investigated, so that the preliminary screening was made from these viewpoints.[1,2)

Utilizing thermodynamic data compilations,[4) we listed up fusions with the latent heat more than 200 kJ/kg and transitions with the latent heat more than 100 kJ/kg. Among thus selected transformations, the materials of low cost less than 1 ¥/kJ (1 ¥ is the Japanese currency.) were choosed. Excellent materials thus selected are NaCl, NaF and $MgCl_2$. Very good materials are urea, $CaCl_2$, KCl, $MgCl_2KCl$, Na_2CO_3, $FeCl_3$, $Na_2Si_2O_5$, Na_2SO_4, NaOH and KOH, while LiF is excellent in the latent heat but not good in its cost. The foolowing materials are also good; polyethylene, Li_2CO_3, P, $CaO \cdot 2B_2O_3$, Al, Zn_2Mg, $FeCl_2$, $MnCl_2$, $AlCl_3$, K_2CO_3, $NaClO_3$, pentaerythritol, $Sr(NO_3)_2$, Mg, NaBr, KBr, NaCN, NaSCN, $SrCO_3$, $ZnSO_4$, $KClO_4$ and Zn.[1) Their working temperatures are from 100°C to 1000°C.

Similar preliminary screening was applied to eutectic mixtures by the same criteria mentioned above. First, eutectic mixtures, whose main component is a substance with large fusion entropy change over 500 J/kgK, are selected from a data compilation of eutectic points and compositions 5) in the temperature range from 80°C to 500°C. These main components are NaF, NaCl, $AlCl_3$, $MgCl_2$, $FeCl_3$, Al, $MnCl_2$, Li_2CO_3, P, LiF, LiOH, NaOH and KOH, and they are all inexpensive materials. Because there are not data of the latent heat of these eutectic mixtures in the data compilation, the heat of fusion is estimated on an assumption of additivity of the entropy change. The same criteria of the latent heat and the material cost were applied, and the candidate eutectic mixtures are selected.

For further evaluations of these candidate materials, thermoanalytical methods, such as DSC, DTA and TG were applied, and the results of these experimental evaluations are described below for some examples.

UREA

Urea is a very inexpensive material, because it is produced in a mass production line as a fertilizer. A typical DSC result is reproduced in Fig. 1, and the estimated heat of fusion is 258.4 kJ/kg. However, large tendency of supercooling is seen and it should be also noted that the heat of fusion on the second heating is decreased remarkably; this fact suggests us low thermal stability. The supercooling tendency can be overcome by formation of eutectic mixtures with KCl and NH_4Cl, and addition of sebaccic acid has also favorable effect. These facts were also confirmed by observing heating and cooling curve with large quanitity of the sample.6)

To observe the thermal stability, TG is applied to the sample.

Typical TG curves are shown in Fig. 2, where the three stage decomposition is observed. Because the first stage decomposition is the cause of the thermal deterioration, this reaction was kinetically analyzed by a method proposed by the present author before.[7] The constant activation energy is obtained along the course of the decomposition, and the average activation energy estimated is 85.0 $\pm$ 0.7 kJ/mol. By using the estimated activation energy, the TG curves were converted to an isothermal type of master curve versus the reduced time,[7] as is shown in Fig. 3, where two actual time abscissas are also shown by calculating from the reduced time and the activation energy. As is clearly shown, the decomposition proceeds in the first order of reaction, and the rate in the working temperature range is fairly high, so that the thermal stability of urea is very low. The low thermal stability of urea can not be improved by the formation of the eutectic mixtures and/or addition of sebaccic acid. It is concluded from these facts that urea is not desirable for the latent heat thermal energy storage materials.

SURFACE-CROSSLINKED POLYETHYLENE

In the same working temperature range as urea, there are other candidate materials, such as eutectic mixtures of $AlCl_3$ or $FeCl_3$. However, these eutectic mixtures are hygroscopic and corrosive, and their heats of fusion may be less than those estimated on the assumption of the additivity, because they tend to form complex ions, which decrease the entropy change of fusion. Thus, the other candidate material, i.e., polyethylene was finally selected.

Polyethylene is inexpensive material with large heat of fusion, and it has been well observed that polyethylene has a little tendency of supercooling. However, there are some drawbacks; low thermal conductivity, high melt viscosity (heat transfer by convection can not be expected) and creeping-up of the melt by high wettability. To overcome these drawbacks, we modified polyethylene by bombardment in argon (or other inert gas) plasma to form crosslinked surface layer. By this modification, polyethylene can retain its form even in the molten state. Similar form-stabilization can also be made by clad with silicone-ethylene copolymer which crosslinks by absorbing moisture after fabrication. These form-stabilizations do not cause any detectable change in the heat of fusion and other thermophysical properties, and they enable to make large heat transfer area to overcome the low thermal conductivity by forming slender rods, thin plates or fine pellets.[3)]

The form-stablized polyethylenes can be used in the direct contact with heat transfer fluids, and the compatibility with the heat transfer fluids was examined by observing thermophysical properties of the polyethylenes which were kept at 150°C in contact with some heat transfer fluids in a sealed DSC container. The results are shown in Fig. 4 and Table 1. It is made clear that the polyethylenes are compatible with ethylene glycol and silicone oil and they are very thermally stable, when they are kept without oxygen.[3)] On the other hand, the hydrocarbon heat transfer fluids, such as alkyldiphenyl and alkyldiphenylethane, decrease the melting temperature but do not change the heat of fusion, because the fluids are solvent of polyethylene to swell and/or dissolve polyethylene.

It was concluded from these facts that surface-crosslinked polyethylenes are very excellent thermal energy storage materials, which can be used in the direct thermal contact with ethylene glycol or silicone oil with large heat transfer area without any costly metal containers. A prototype latent thermal storage equipment by using the polyethylene is described below.

After experimental test with a lab-scale thermal storage apparatus, we designed and constructed the prototype polyethylene thermal storage equipment, as is shown in Fig. 5. The diameter and the height of the storage column are 60 cm and 2m, respectively. The form-stable polyethylene rods (4 mm in diameter and 450 mm in length) are fixed with aluminum honeycombs and four sets of the rods are set in the coumn. The total weight of the polyethylene is 281 kg, and the storage capacities are 50.6 MJ with the latent heat of polyethylene, 0.72 MJ/K with sensible heat of polyethylene and 0.79 MJ/K with sensible heat of ethylene glycol. A typical performance of the equipment in discharging mode is reproduced in Fig. 6. In this experiment, ethylene glycol kept at about 143°C was first flowed from the top to store the heat, and after complete charging up, cool ethylene glycol kept at 105°C was introduced from the bottom. The stored heat was extracted from the equipment with heated ethylene glycol from the top. As is clearly shown, the temperature of the released heat is maintained above the crystallizing temperature of the polyethylene, and the unique feature of the latent thermal energy storage is fully realized.[8)]

PENTAERYTHRITOL

Pentaerythritol is a unique material, because it undergoes crystalline transition at 188°C with the heat of transition over 300 kJ/kg, so that it is still in the crystalline state even in the charged state. First, DSC was applied to observe its transition behavior, and typical DSC curves are shown in Fig. 7. Supercooling tendency is observed, and the nucleation-controlling transition seems to occur in cooling mode, as is deduced from the shape of the DSC curves. However, the supercooling tendency is not so large as in urea, and it is not considered that the tendency is a serious drawback in utilizing it in the latent thermal storage. Because pentaerythritol is an organic material, its low thermal conductivity is also a serious drawback as in polyethylene latent thermal storage. Taking into accounts of the crystalline transition, we have made an attempt to use powder of pentaerythritol in a slurry with some compatible heat transfer fluids, to overcome the drawback of the low thermal conductivity.

To observe the compatibility with heat transfer fluids and the thermal stability of the slurry, the similar measurements to polyethylene were made at 200°C in sealed glass containers. The slurries were sealed in the glass containers and kept at 200°C for long time. DSC measurements of the slurries were made intermittently with the sealed glass containers as the DSC sample containers. Similar results to polyethylene were obtained, and the hydrocarbon heat transfer fluids are very good for the purpose.[9)]

A lab-scale latent thermal storage apparatus was designed and assembled. The apparatus is a shell-and-coil type heat exchanger, and the slurry was put in the shell. To enhance the heat transfer between the slurry and other heat transfer fluid flowing in the coil for charge and discharge, the slurry was agitated. The agitation is also effective to enhance the heat transfer between the pentacrythritol powder and the heat transfer fluid within the slurry. Similar performance, especially the constancy of the temperature of the released heat, was observed, but it is somewhat inferior to that of polyethylene, because temperature stratification can not be formed as in polyethylene, but the temperature of the slurry becomes uniform by agitation. Another serious problem discovered is adherence of pentaerythritol powder in the charged state to the walls of the shell and the coil, when the agitation is insufficient, because pentaerythritol above 188°C is plastic cystal.[10] We are looking for some devices to overcome this problem.

BINARY EUTECTIC MIXTURES OF ALKALINE HYDROXIDES

Binary eutectic mixtures of LiOH, NaOH and KOH are also very promising materials in the results of the above-mentioned preliminary screening. However, from simultaneous TG and DTA measurements, it became clear that trace of moisture has remarkable and harmful effect on the fusion and its heat. One example is reproduced in Fig. 8. In this figure, the endothermic peaks about 90°C decrease and the peak at 248°C due to the reported transition increases along with the weight loss by repeated heating from the curve a to the curve e. These facts suggest us importance of dehumidifying the materials in the practical applications.

After sufficient dehumidification, DSC measurements of the binary eutectic mixtures were made, and a typical result is reproduced in Fig. 9. The other two binary mixtures show only one peak of melting. The temperatures and the heats of fusion and transition are 184°C, 214°C and 330 kJ/kg for LiOH-NaOH (30 - 70 mol %), 222°C and 184 kJ/kg for LiOH-KOH (29 - 71 mol %) and 165°C and 172 kJ/kg for NaOH-KOH (50 - 50 mol %). Considering large hygroscopic nature of KOH and high cost of LiOH, the two mixtures, i.e., NaOH-KOH and LiOH-NaOH, are promising from thermoanalytical evaluations.[11] However, they are very corrosive and even stainless steel is found to be corroded in these molten mixtures, so that some devices are necessary for practical application of these mixtures.

BINARY MIXTURES AND COMPOUNDS OF NaOH WITH $NaNO_3$ OR $NaNO_2$

There are two compounds and three eutectic mixtures in the binary system of NaOH and $NaNO_3$, while one compounds and two eutectic mixtures in the binary system of NaOH and $NaNO_2$. All these mixtures and compounds have their melting points in a temperature range from 230°C to 280°C, where there are not other candidate materials. For these mixtures and compounds, trace of water has also much influence on their thermophysical properties, and DSC was applied to these materials after enough dehumidification. The results are listed up in Table 2, where ΔT is difference in the extrapolated onset temperature between heating and cooling measurements and it is a measure of supercooling tendency. Except a few materials, they have not so high tendency of supercooling as urea, and they are promising materials for latent thermal storage in the above temperature range.12) In contrast with the eutectic mixtures of hydroxides, carbon steel is fairly resistant to the corrosion in the melt of these materials and stainless steel is inferior to carbon steel in corrosion-resistance. It is elucidated from our preliminary technological feasibility study that the materials, especially a binary eutectic mixture of $NaOH$-$NaNO_3$ (81.5 - 18.5 mol %), can be used in latent thermal storage in nuclear power plants; the heat from nuclear reactors, especially pressurized water type reactors, is stored as the heat of fusion of the materials in the night, and the heat released from the materials is used for peak electric power generation in the daytime, when the electric consumption increases remarkably.13)

CONDLUDING REMARKS

The latent thermal storage has unique feature of constant temperature heat release, as is illustrated in the performance of the polyethylene latent thermal storage equipment, and it has high energy density. The materials, equipments and technology with various working temperatures will be developed by further research and development. The technology is useful in solar energy utilization, waste heat recovery and load levelling of power plants, and it may be also useful in thermal management in space stations.

Thermoanalytical methods, such as DSC, DTA and TG, are very powerful tools in experimental evaluations of important characteristics, including the temperature of transformation, the latent heat, the specific heat capacity, the dynamic behavior of transformation, the thermal stability and the compatibility. They will be further applied to the high temperature materials, such as chlorides in a temperature range from 300°C to 500°C, carbonates in a temperature range above 500°C and fluorides in a higher temperature range.

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Table 1

Effect of surface-crosslinking, heat transfer media and aging on melting temperature [a], crystallizing temperature [a] and heat of fusion

(a) Untreated polyethylene

Heat transfer medium	None		Silicone		Alkyldiphenyl	
Aging time at 150°C (h)	0	500	0	500	0	500
Heat of fusion ($J g^{-1}$)	226	211	233	220	232	232
Melting temp. (°C)	128	131	128	128	106	108
Crystallizing temp (°C)	125	128	124	125	109	110

(b) Surface-crosslinked polyethylene

Heat transfer medium	None	Silicone		Alkyl-diphenyl		Alkyldi-phenylethane	
Aging time at 150°C (h)	0	0	600	0	600	0	600
Heat of fusion ($J g^{-1}$)	221	228	225	233	195	239	221
Melting temp. (°C)	126	127	127	112	107	112	111
Crystallizing temp. (°C)	124	123	123	110	109	110	111

Heat transfer medium	Ethylene glycol		Caloria HT	
Aging time at 150°C (h)	0	600	0	600
Heat of fusion ($J g^{-1}$)	225	207	219	212
Melting temp. (°C)	128	128	115	116
Crystallizing temp. (°C)	123	123	112	114

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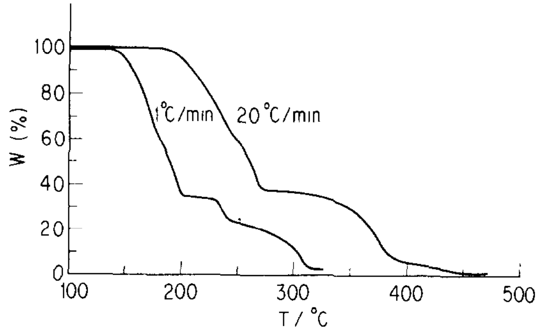
[a] The temperatures are the extrapolated onset temperatures.

Table 2

Thermophysical properties of mixtures and compounds of NaOH with $NaNO_3$ and $NaNO_2$

Materials	Composition mol %	T_m* °C	ΔT °C	ΔH kJ/kg
$NaOH-NaNO_3$	81.5-18.5	259	2	279
	59-41	267	35	273
	28-72	248	46	222
$NaOH \cdot NaNO_3$	----	272	42	251
$2NaOH \cdot NaNO_3$	----	272	60	284
$NaOH-NaNO_2$	73-27	239	15	285
	20-80	235	3	285
$NaOH \cdot NaNO_2$	----	267	45	294

* The melting temperatures are the extrapolated onset temperatures.



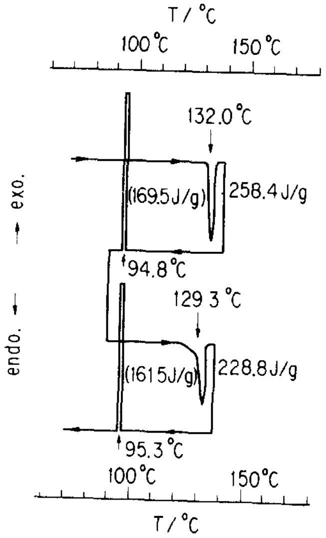
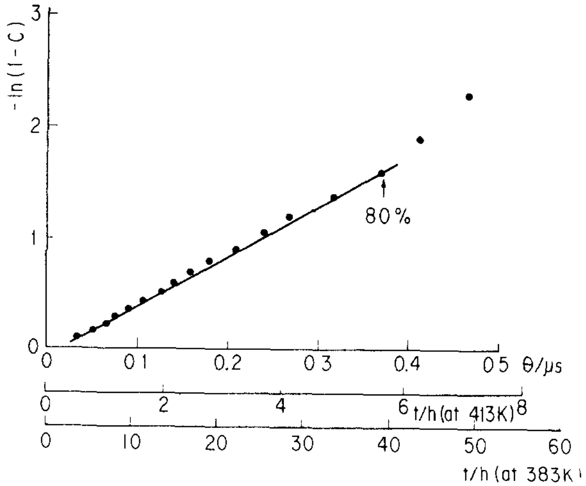


Fig. 1. Typical DSC curves of urea.

Fig. 2. Typical TG curves of urea

Fig. 3. Experimental master curve of first decomposition of urea. (converted from TG curves on assumption of first order reaction.)



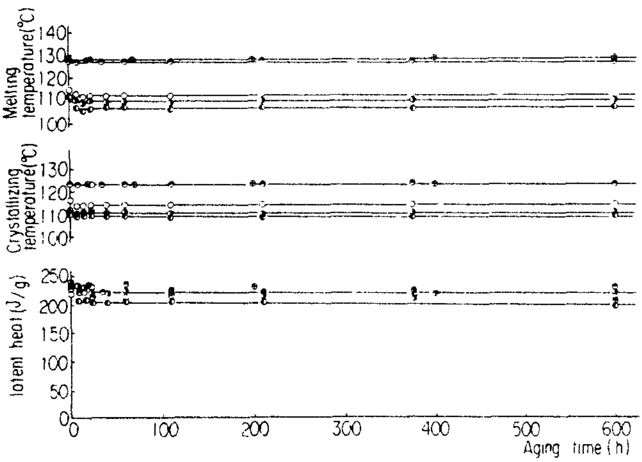


Fig. 4. Changes in thermophysical properties of surface-crosslined polyethylene. ◓ polyethylene without heat transfer fluids; ● Polyethylene with silicone oil; ◐ polyethylene with alkyldiphenyl; ◑ polyethylene with alkyldiphenylethane; ○ polyethylene with Caloria HT; ⊕ polyethylene with ethylene glycol.

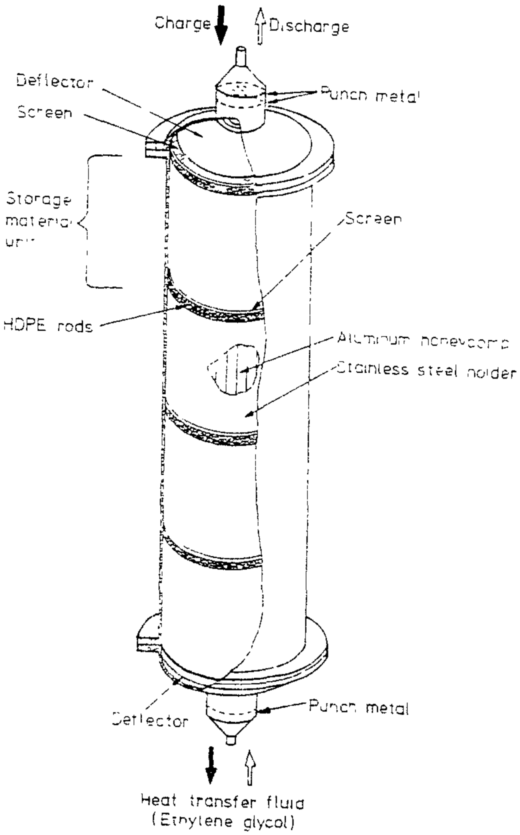


Fig. 5. Polyethylene latent thermal storage column.

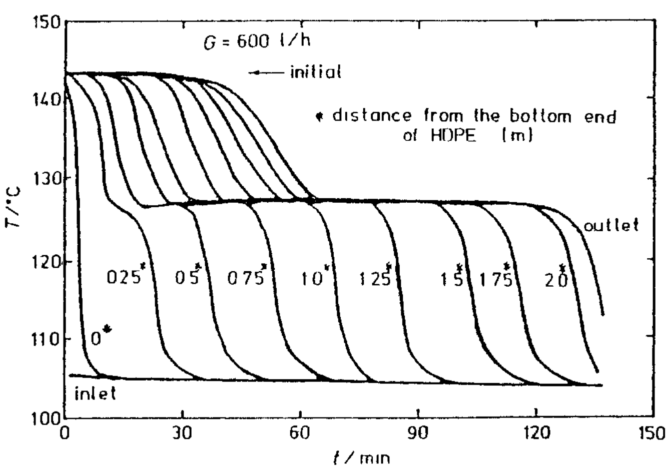


Fig. 6. Discharging performance of polyethylene latent thermal storage equipment.

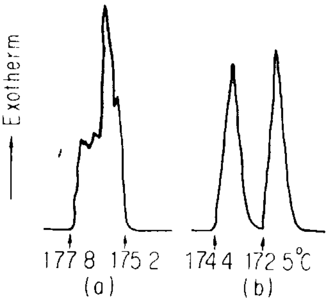


Fig. 7. Typical DSC curves of pentaerythritol in cooling mode.

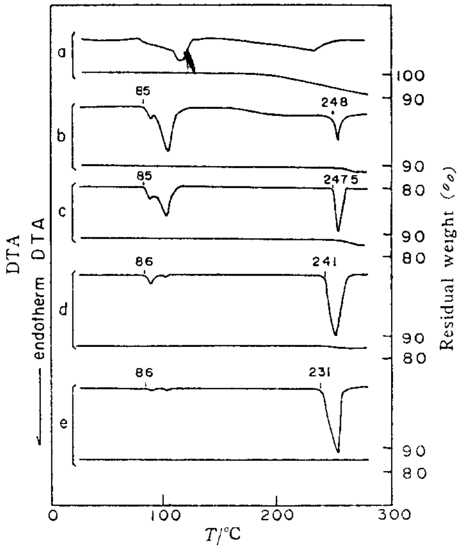


Fig. 8. TG-DTA curves of KOH showing effect of dehumidification.

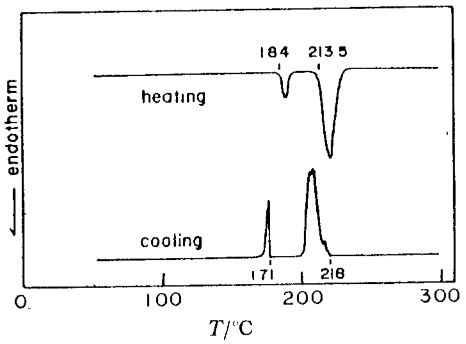


Fig. 9. DSC curves of LiOH-NaOH eutectic mixture.