INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONE: 2240-1
CABLE: CENTRATOM - TELEX 460392 - I

H4.SMR/193 - 31

"COLLQUE INTERNATIONAL SUR LA SCIENCE DES MATERIAUX POUR L'ENERGIE".
(26 août - 11 septembre 1986).

# " LOW TEMPERATURE LATENT HEAT STORGE : RECENT DEVELOPMENTS OF CALCIUM CHLORIDE COMPOUNDS AT LOW TEMPERATURE (20 C - 30 C).

J. Guion
University of Nice
Valbonne, France

Presented by A. Jaffrin

---

Ces notes de recherche provisiores, sont destinées aux participants. Eventuellement, d'autres copies seront disponibles au bureau 231.

are presented in references ( 2) and ( 6). These facts are illustrated in figure 1 where the advantages of PCM over water (only sensible heat available), for low temperatures, are clearly outlined.

. MELTING AND COOLING PHENOMENA : illustration with two salt hydrates.

Thermodynamic behaviour of materials selected can be learned by examining the phase diagram, temperature versus composition, for salt hydrates. However as shown for the two following examples, $Na_2SO_4$, 10 $H_2O$ (Glauber's salt) and $CaCl_2$, 6 $H_2O$,actual fusion and solidification processes can be more complex than expected.

1) Melting and cooling of Sodium sulfate decahydrate.

Sodium sulfate decahydrate ($Na_2SO_4$, 10 $H_2O$) (Glauber's salt) received much attention as heat storage material. When melted at the temperature of 32.4°C, a peritectic decomposition reaction occurs (point P [illegible] phase diagram partly reproduced in figure 2) :

$$Na_2SO_4,\ 10\ H_2O \rightarrow Na_2SO_4\ (s) + \underset{\text{(saturated solution)}}{Na_2SO_4\ (aq)}$$

Because of the higher density of the solid $Na_2SO_4$, separation from the saturated solution happens and accumulation of $Na_2SO_4$ (s) is observed, as the temperature is raised over the melting point corresponding to P.
When cooled, the same sample would have to freeze at the same temperature, 32,4°C. Two different known phenomena occur :

a) Supercooling.

Germs of crystals (embryos of $Na_2SO_4$, 10 $H_2O$ (s))are not formed with a sufficient rate, or kinetics of development of cristallites from germs is too slow; both lead to a supercooling of the solution, under the phase transition temperature corresponding to equilibrium conditions.

b) Segregation.

Considering that there is no supercooling, when cooled at 32,4°C, the reversible peritectic reaction is not complete, because water diffusion through solid $Na_2SO_4$ suffers from kinetics limitations (depending upon scale of solid particles, formation of a crust at the interface solid-saturated solution, concentration gradients,..).
Finally considering several melting-freezing cycles, a larger quantity of inactive $Na_2SO_4$ is formed and does not recombinates with water.
This evidently results in decreasing sharply the amount of actually available latent heat.
This phenomenon called segregation is very common for salt hydrates which present an incongruent melting phase-diagram, the solid segregating salt being either the anhydrous form or another hydrated form.

For the much studied Glauber's salt, many investigators claimed successful attempts in preventing gross segregation. Numerous techniques have been tried such as use of thickening agents (10), gellation (11) (13), chemical encapsulation (12) (13), mechanical stirring or shaking (14) (15) (16). However many disapointing experiences have been encountered (11) and new recent developments have not been tested for enough time, or reported as really operative for large scale applications.

Figure (3) redrawn from reference (11) show how important can be the segregation effect.

TABLE I

| Compounds | Melting point or Solid-solid transition temperature °C | Heat of transition J.g$^{-1}$ |
|---|---|---|
| 1) Inorganic salts | | |
| LiCl | 607 | 468 |
| NaCl | 800 | 476 |
| KCl | 770 | 360 |
| $NH_4Cl$ | 185 | 75 |
| $MgCl_2$ | 714 | 452 |
| $CaCl_2$ | 772 | 255 |
| $LiNO_3$ | 251 | 389 |
| $NaNO_3$ | tr 276 | 46 |
| | f 310 | 188 |
| $KNO_3$ | tr1 128 | 58 |
| | tr2 160 | 37 |
| | f 337 | 117 |
| $NaCH_3CO_2$ | 328 | 226 |
| 59 % LiCl-41 % KCl | 352 | 243 |
| 44 % NaCl-56 % FeCl | 158 | 167 |
| LiOH | 471 | 876 |
| 2) Salts Hydrates | | |
| $MgCl_2$, 6 $H_2O$ | 117 | 169 |
| $CaCl_2$, 6 $H_2O$ | 29 | 191 |
| $Mg(NO_3)_2$, 6 $H_2O$ | 89 | 163 |
| $Na_2SO_4$, 10 $H_2O$ | 32,4 | 244 |
| $LiNO_3$, 3 $H_2O$ | 30 | 296 |
| $Na_2S_2O_3$, 5 $H_2O$ | 48 | 200 |
| $Na_2HPO_4$, 12 $H_2O$ | 36,5 | 279 |
| $Ba(OH)_2$, 8 $H_2O$ | 78 | 266 |
| $NaCH_3CO_2$, 3 $H_2O$ | 58 | 289 |

TABLE I (continued)

| Compounds | Melting temperature or solid-solid transition temperature °C | Transition heat J.g$^{-1}$ |
|---|---|---|
| 3) Organic materials | | |
| p. chlorobenzoic acid | 240 | 206 |
| Acetic acid | 17 | 201 |
| Stearic acid | 69 | 202 |
| Naphtalene | 80 | 148 |
| Urea | 133 | 251 |
| paraffin | 57 | 209 |
| paraffin | 62 | 209 |
| Palmitic acid | 64 | 185 |
| Capric acid | 36 | 153 |
| Lauric acid | 49 | 177 |
| n-eicosane | 37 | 247 |
| 67,1%Naphtalene<br>32,9 Benzoic acid | 67 | 123 |
| 66,6 % urea<br>33,4 $NH_4Br$ | 76 | 151 |
| 4) Plastic cristals | | |
| penta-erythritol | tr 184 | 250 |
| | f 256 | 25 |
| pentaglycerine | tr 86 | 161 |
| | f 195 | 28,5 |
| neopentylglycol | tr 44 | 125 |
| | f 130 | 38 |
| 2amino-2methyl,1-3 propanediol | tr 89 | 240 |
| | f 102 | 28 |
| 2amino-2hydrosymethyl 13,propanediol | tr 138 | 284 |
| | f 167 | 25 |

Several large scale-applications have been realised with various configurations (32) (33) (35) (36) (37).

## B. RECENT DEVELOPMENTS OF MULTI-COMPONENTS SYSTEMS RICH IN CALCIUM CHLORIDE.

For building applications and greenhouse developments there is a need for PCM, melting at temperatures in the range 18°C-25°C. The idea followed was to take Calcium Chloride hexahydrate as the basic component and to try several addittives in order to get lower melting temperatures.

1) First trials concerned use of the "extra-water principle" (29) (38), but again a sharp decrease of expected latent heat is observed.

2) Pseudo-Ternary system ($CaCl_2$, 6 $H_2O$), KCl, $NH_4Cl$.

Following one scarce observation about two not-well defined compositions of ($CaCl_2$, 6 $H_2O$), $NH_4Cl$, KCl mixture (39) we went through the exploration of this pseudo-ternary mixture.

Figure 7 shows the lines along which we were working , either with constant Calcium chloride hexahydrate (X $CaCl_2$ = Ct) or with constant ratio of number of moles of Potassium Chloride versus Ammonium Chloride (y = Ct). Moreover,the worked area is within the estimated solubility limits of both anhydrous salts, indicated (not precisely known) on the figure. This system has been studied considering that ($CaCl_2$, 6 $H_2O$) was a perfectly definite phase.

Solutions are prepared from pure compounds ($CaCl_2$, 2 $H_2O$), KCl and $NH_4Cl$, purchased from Carlo Erba. We first dissolved anhydrous salts KCl and $NH_4Cl$ in the necessary quantity of water (endothermic step) to prepare $CaCl_2$, 6 $H_2O$ from the dihydrate $CaCl_2$, 2 $H_2O$ (exothermic step). Neither nucleating agent, nor thickener are added.
The solutions are then tested for their thermal performances by differential scanning calorimetry (DSC). All the samples are taken out at a fixed temperature of 32°C, and rapidly frozen at - 20°C.
Calorimetric curves giving specific heat at constant pressure Cp, versus temperature are recorded on heating, at a slow rate, 2 or 3°C per hour. Integrated curve giving the enthalpy versus temperature are automatically obtained with the programm associated with the calorimeter, a DSC 111 from SETARAM, further details are given in (38).

The results may be analysed following the evolution of the Cp curves, for the signals are closely related to the corresponding phase diagram. Figure (8) shows the evolution of Cp signals along one value of X $CaCl_2$, 6 $H_2O$ constant, with varying y = n KCl/n $NH_4Cl$, ratios. As we may observe though,the Cp signals are quite different, the total amount of heat absorbed during melting is approximately constant, for y varying from 1.10 to 0.44,for X = .75.
The shape of the Cp curves allows some predictions about the possible existence of an eutectic valley. Around the composition of MU 131, the coalescence of the two peaks is not far from being complete. A more detailed investigation allowed us to locate a precise area on the pseudo-ternary diagram. On figure (9),corresponding to compositions indicated table II, we may precise further this point.
We may observe the high sensitivity of Cp signals to slight changes of composition (this curves are highly reproducible). Moreover the melting temperatures, got from intersection of basis line with extrapolated tangent at the first inflexion point of Cp curves, give precisely 22,5°C, in all cases.
When cycled, compositions corresponding to MU 124 or MU 125 give extended horizontal levels during melting, or cristallising steps, at least for the first cycles.

As we already mentionned, segregation may be soon observed after ten (or even less) cycles. Supercooling conditions are also easily met. This makes compulsoryfor industrial applications of long term to introduce diatomites as stabiliser. Solutions prepared with technic $CaCl_2$ and diatomites have been experimented as stable (40).

TABLE II

| | X $CaCl_2$, 6 $H_2O$ | y = n KCl / n $NH_4Cl$ |
|---|---|---|
| MU 131 | .750 | .429 |
| MU 124 | .747 | .399 |
| MU 125 | .740 | .383 |
| MU 126 | .740 | .445 |
| MU 127 | .759 | .385 |

We have to underline how difficult it is to identify clearly what are exactly the solid phases in equilibrium, in the transition zone. Some experimental X-Ray work is still going on, with emphasis on avoiding moisture and following the materials through the melting phase-change transition (22,5°C - 25°C).

One way mentionned to avoid the segregation problem, or more correctly to slow it down, is to operate outside the precise peritectic composition. This has been quoted as "the extra-water principle" (17), and experimented several times (18) (19). A recommended composition (18) is 30 % $Na_2SO_4$ by weight ; starting with a mixture corresponding to the composition of point N on figure 2, and rising temperature will not give the peritectic decomposition precedently mentionned, at least for temperatures under 40°C. If we now undertake the reverse path, and cool the liquid which corresponds to point Q we should begin to nucleate the decahydrate when the temperature is that of M, and this salt is separating from the liquid ; at point N, we have the composition of the liquid solution given by R, and the amount of decahydrate cristallised may be calculated by the lever rule along RND.
Unfortunately the amount of heat released is very strongly affected by departure from the peritectic composition (as much as 40 % for the first cycles).

2) Calcium chloride hexahydrate.

Figure (4) reproduces part of the phase diagram $CaCl_2$-$H_2O$, showing the presence of two compounds $CaCl_2$, 6 $H_2O$ (hexahydrate A) and $CaCl_2$, 4 $H_2O$ (tetrahydrate B). The tetrahydrate is known under three allotropic forms, the stable one being the α-variety. Broken lines represent metastable lines for the three tetrahydrate forms and the calcium choride di-hydrate. The liquidus branches of hexahydrate and tetrahydrate (α-allotropic form) join at a peritectic point P, which means that for a solid having the composition of A, if melted and then cooled we may observe formation of tetra-hydrate B. Then as the density of B is higher than that of A, we should have the segregation phenomena.

As for the Glauber's salt problem, many studies concerning nucleation and suppression of segregation effects have been realised.
Whithout nucleating agents, Calcium chloride hexahydrate may severely supercool. A variety of nucleating agents have been tested and may play a role in preventing supercooling (20) (21) (22) (23) (24) (25). Most of mentioned nucleating agents are naturally present in the technical calcium chloride. One of them, strontium chloride hexahydrate, is an epitaxial agent (crystal parameters very near to that of calcium chloride hexahydrate, which may explain its possible nucleating function), but as it is soluble in calcium chloride hexahydrate, it may also act as modifying the phase diagram (26). Large controversies exist on the exact rôle, and the true responsible for supercooling suppression (26) (27) (28).

As the peritectic composition is very near the composition of hexahydrate, this compound is often said as being "quasi-congruent melting". In fact this may only be obtained with additives which modify the phase diagram (26) to (28).
Among the most effective are strontium chloride hexahydrate and potassium chloride, which both affect the melting temperature and the relative position of peritectic and calcium chloride hexahydrate. However it is not completely sure that after many cycles, gradually increasing amounts of calcium chloride tetrahydrate are not formed. Another way of working is to use the "extra-water principle" as explained before, with some losses of latent heat, and a lowered melting temperature (29).
As for the glauber's salt, many thickening agents have been tried with very little or moderate success (see reference 2 for instance), except for one discovered in our laboratory (30). It consists in special kind of diatomeous earth, "synedra" variety, with needle form along which arrays of holes-about 50 angstroëms diameter, about 10 per array for 5000 Å length needle - are regularly disposed. The effectivness of such stabilising agent has been clearly demonstrated and solar houses are equiped with and have been operating without problems for the last 8 years
The rôle of diatomites is not completely understood yet, but it is generally thought as being two fold:

- mechanical dispersion, though their distribution preventing any settling down of tetrahydrate, and then allowing its eventual redissolution, if ever formed.

- microporous properties, favoring preferential nucleation of hexahydrate and orienting the cristalline growth of this compound.

The composition of the mixture $CaCl_2$-$H_2O$ and diatomites, plus nucleating agents, has been patented (30) and the product is commercially sold under the name "Chliarolithe". Actually it is presented by the SOLVAY Chemical society under a ready-to-make mix (dehydrated mixture of $CaCl_2$ + diatomites) in plastic bags of 25 kg, under the trade name of "Casotherm" (31).

The thermal performances of a moderately good sample of chliarolithe (a little excess of water) and pure calcium chloride hexahydrate (freshly prepared, and rapidly congelated at - 20°C) are compared in figure 5 (Cp versus temperature) and figure 6 (ΔH versus temperature).

(1) RALDOW W.M. and WENTWORTH W.E., Chemical heat pumps : a basic thermodynamic analysis.
Solar Energy, 23 (1979).

(2) TELKES M., Phase change thermal storage/a comprehensive look at developments and prospects, MONEGON Ltd report M 105, September 1980.

(3) GUION J., SAUZADE J.D. and LAÜGT M., Critical examination and experimental determination of melting enthalpies and entropies of salt hydrates.
Thermochimica Acta, 67 (1983), p. 167-179.

(4) LANE G.A., Low temperature heat storage with phase change materials, The Int. J. of Ambient Energy, Vol 1, N° 3, (1980).

(5) ABHAT A., Low temperature latent heat thermal energy storage : heat storage materials, Solar Energy, Vol 30, N° 4, (1983) p. 313-332.

(6) ABHAT A., Short term thermal energy storage, Revue Phys. Appl., 15, (1980), p. 477-501.

(7) STAVELEY L.A.
Ann. Rev. Phys. Chem., Vol 13, 351 (1962).

(8) CHANG S.S. and WESTRUM E.F.
J. Phys. Chem. 64, 1547 (1960).

(9) MARSHALL J.G., STAVELEY L.A. and GUPTA A.K. Trans. Far. Soc. Vol 45, 50 (1949).

(10) TELKES M., US Patent 3, 986, 969 (1976).

(11) MARKS S.B., An investigation of the thermal energy storage capacity of Glauber's salt with respect to thermal cycling. Solar Energy Vol 25, 255 (1980).

(12) KENT P.J. and PAGE J.K., U.S. Patent 4, 209, 613 (1980).

(13) TELKES M., U.S. Patent 4, 187, 189 (1980).

(14) HERRICK C.S., U.S. Patent 4, 154, 292 (1979).

(15) EDIE D.D., MELSCHEIMER S.S. MULLINS J.C. and MARRA J.F., Sun II : Proceedings of the ISES Silver jubilee congress, ATLANTA, May (1979) p. 640.

(16) GREENE N.D., U.S. Patent 4, 109, 702 (1978).

(17) FURBO S. and SVENSDEN S., Report on heat storage in a solar heating system using salt hydrates, Technical University of DENMARK (July 1977).

(18) BISWAS D.R., Thermal energy storage using sodium sulfate decahydrate and water, ISES Meeting, LOS ANGELES, California (July 1975) and Solar Energy, Vol 19, p. 99-100 (1977).

(19) FURBO S., Heat storage units using salt hydrate, Sunworld, Vol. 6, N° 5, (1982).

(20) DANILIN V., DOLESOV A., PETRENKO R. and SHAPOSHNIKOVB, U.S.S.R. Patent 568, 669 (1977).

(21) KAI J., KIMURA H. and MUTOH K., Japanese Patent Kokai 53-191, 183 (1978).

(22) ISHIHARA H., NONOGAKI S., Japanese Patent 55-9, 596 (1978).

(23) MIYOSHI H. and TANAKA K., Japanese Patent Kokai 53-191, 183 (1978).

(24) SCHRODER J. and GAWRON K., U.S. Patent 4, 189, 394 (1980).

(25) LANE G.A. and ROSSOW H.E., U.S. Patent 4, 272, 390 (1981).

(26) CARLSSON B., STYMNE H. and WETTERMARK G., An incongruent heat-of-fusion system $CaCl_2$, 6 $H_2O$ - made congruent through the modification of the chemical composition of the system. Solar Energy 23, 343-350 (1979).

3) Quaternary compositions with $CaCl_2$, $H_2O$, KCl and $NH_4Cl$.

Results mentionned here were initiated by some observations related to experiments made with technical products, where the exact ratio of water to calcium chloride was not correctly adjusted to get the hexahydrate composition. repeated experiments, with lack of water up to 10 % of the molar composition were performed. Again, multiple forms of Cp signals - generally two peaks - are obtained, but within a narrow domain of compositions, we observed the probable formation of an eutectic compound, with a heat content of about 190 J/g, and a melting temperature of 23,9°C (41). Figure (10) shows the results obtained for a typical composition corresponding to n $CaCl_2$ = .430, n $H_2O$ = 2.44, n KCl = .040 and n $NH_4Cl$ = .101. This composition has been tested for stability towards segregation. With a water deficit of 5,3 % compared to the hexahydrate composition, we could not trigger any indesirable tetrahydrate even by adding some external tetrahydrate germs

These facts cannot be interpreted correctly without a careful X-ray analysis of the solid phases. However, it seems that several liquidus surfaces of the (unknown) multi-component phase diagram may present intersections with low slopes, enabling the existence of local eutectics with temperatures very near to each other. This makes the necessary cristallographic work a very challenging one though not easy to perform.

4) Reciprocal solutions of hydrated calcium chloride with alkali and alkaline-earth nitrates.

As the results under this section are patent-pending, we can only underline the main facts observed.

Solutions, stabilised with diatomites and containing calcium chloride hexahydrate, alkali and/or alkaline-earth nitrates have been prepared and lead to reversible phase-change behaviour.
The Cp curves (figure 11) present generally two well defined peaks, corresponding to two different phases, with very near melting points. One of the phase can be caracterised as an eutectic, and presents a melting temperature of 19,7 ± 0.5°C (first peak). The $\Delta H$ content (figure 12) is around 170 $J.g^{-1}$.

These values are strongly dependent of the compositions, and a detailed examination will be published in a near future.

Acknowledgements : We want to express our thanks to M. LAUGT, M. TEISSEIRE and A. JAFFRIN, for their fruitful collaboration, and to C. UBALDI, A. ROUSTAN, A. COUVE, F. UBALDI and D. MORICE for their technical assistance.

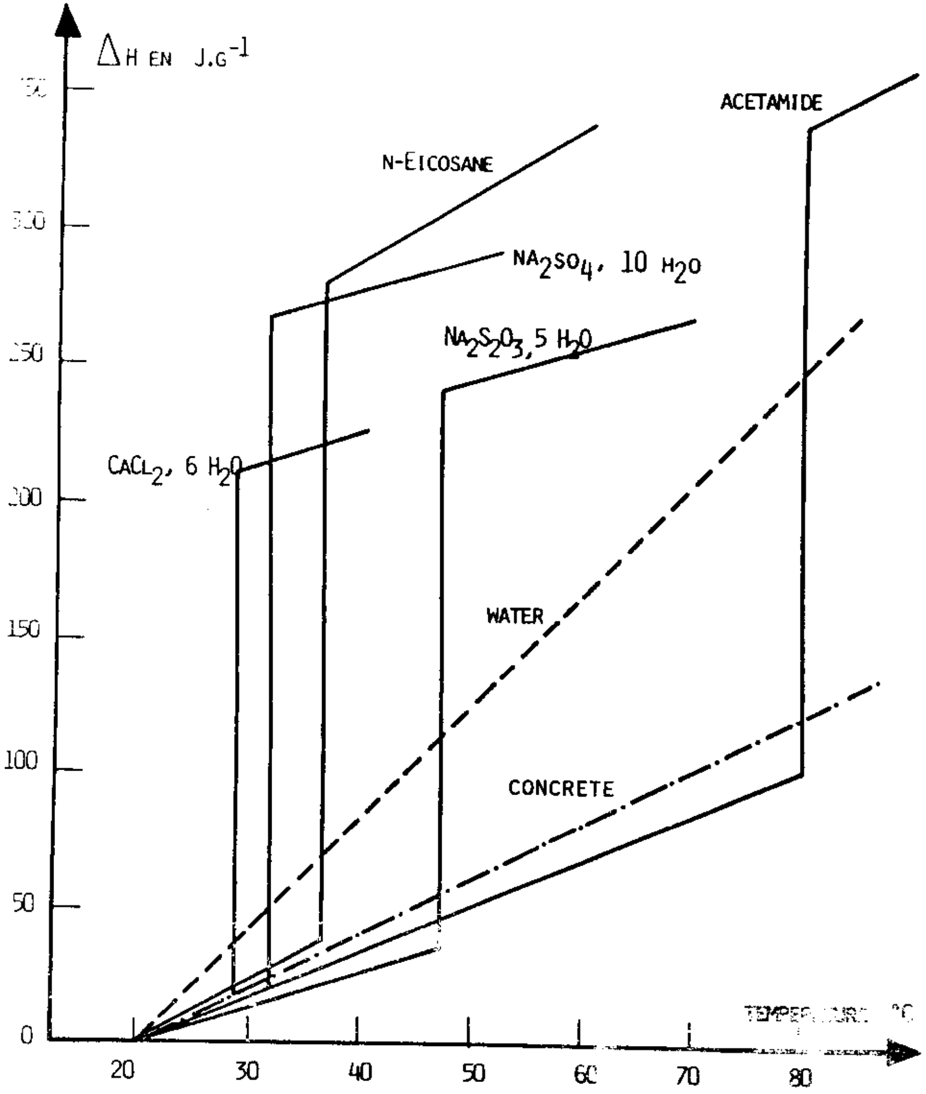


FIG. 1 . TOTAL HEAT CONTENT OF SOME MATERIALS REFERRED TO A BASIC TEMPERATURE OF 20°C.

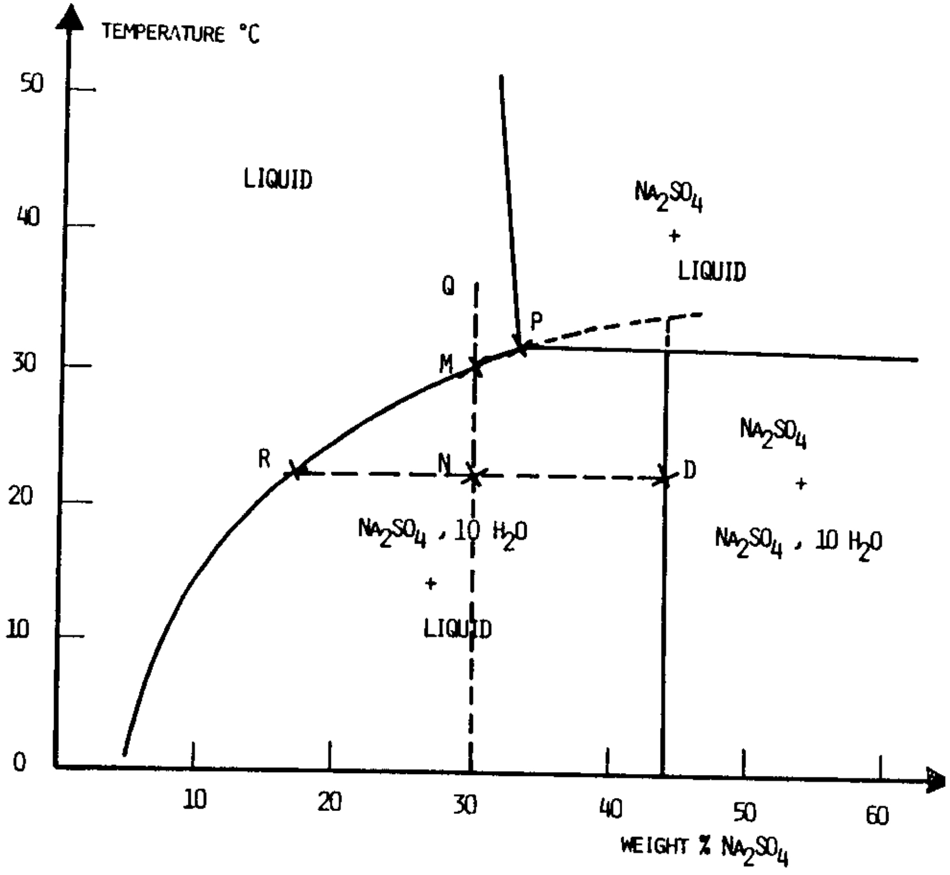


FIG 2. PART OF THE PHASE DIAGRAM $Na_2SO_4 - H_2O$ .

(27) LANE G.A., Adding strontium chloride or calcium hydroxyde to calcium chloride hexahydrate heat storage material. Solar energy Vol 27, p. 73-75 (1981).

(28) FEILCHENFELD H., FUCHS J. and SARIG S., A calorimetric investigation of the stability of stagnant Calcium Chloride Hexahydrate melt, Solar Energy, Vol 32, N° 6, p. 779-784 (1984).

(29) JAFFRIN A. and CADIER P., Latent heat storage applied to horticulture, La Baronne Solar greenhouse. Solar Energy, Vol. 28, N° 4, p. 313-321 (1982).

(30) SCHNEIDER M., SYLVAIN J.D., BERGER X., JAFFRIN A., BOURDEAU, ANVAR-CNRS French Patent N° 79 13296, (1977) and European patent 0, 019, 573 (1979).

(31) DEMILIE P. and MATHIS P., European patent (19 Octobre 1983) 0, 091, 701 A1.

(32) BERGER X., HENRY J.J. Performance of the Grimaud solar house, International Symposium on solar energy, Izmir, TURKEY (August 1979).

(33) BOURDEAU L., JAFFRIN A., Latent heat diode wall on solar energy. International Symposium on solar energy, Le Caire, (June 1978).

(34) JAFFRIN A., HENRY J.J., Mur diode à chaleur latente dans une architecture traditionnelle. International solar architecture conference, Cannes (FRANCE) (December 1982).

(35) PETITCOLLOT C., A mediterranean latent heat solar house in Le Tignet. PLEA N° 2 (CRETE) (June-July 1983), p. 123.

(36) BOURDEAU L., Utilisation d'un matériau à changement de phase dans un mur Trombe sans thermocirculation. Rev. Phys. Appl. 17, p. 633-642, (1982).

(37) DEVAL J.C., Latent heat venetian blind, PLEA N° 2 (CRETE) (June-July 1983) p. 409

(38) GUION J., PELOUS E., TEISSEIRE M. and LAÜGT M., Mise au point et évolution du comportement thermique de mélanges au moins quaternaires riches en chlorure de calcium hexahydraté, pour des stockages entre 18 et 25°C. A.F.C.A.T., Calorimétrie et Analyse thermique, Montpellier, Vol. XVI p. 462-469. (1985).

(39) MEISINGSET K.K. and GRONVOLD F., Latent heat storage in salt hydrates. Solar benefits evaluated, Techniques and results evaluated, Birmingham (September 1982).

(40) JAFFRIN A., LAÜGT M., GUION J., PELOUS E., Belgian Patent 9002448, SOLVAY (17/5/85).

(41) JAFFRIN A., LAÜGT M., GUION J., PELOUS E., Belgian Patent 9002449, SOLVAY (17/5/85).

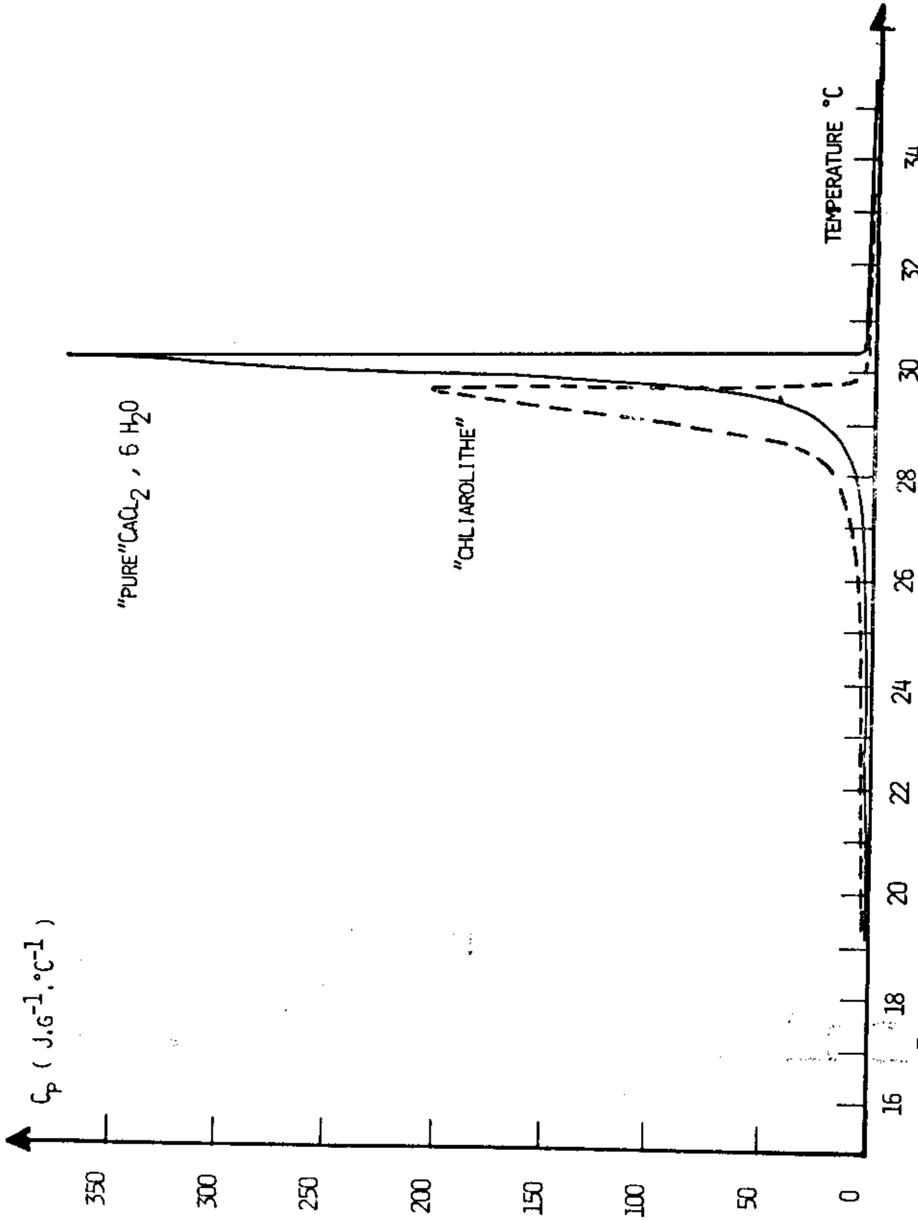


FIG. 5. COMPARISON OF SPECIFIC HEAT $C_P$ VARIATIONS WITH TEMPERATURE, FOR PURE CALCIUM CHLORIDE HEXAHYDRATE AND A MODIFIED ONE BY ADJONCTION OF NUCLEATING AGENTS AND DIATOMITES AS THICKENER.

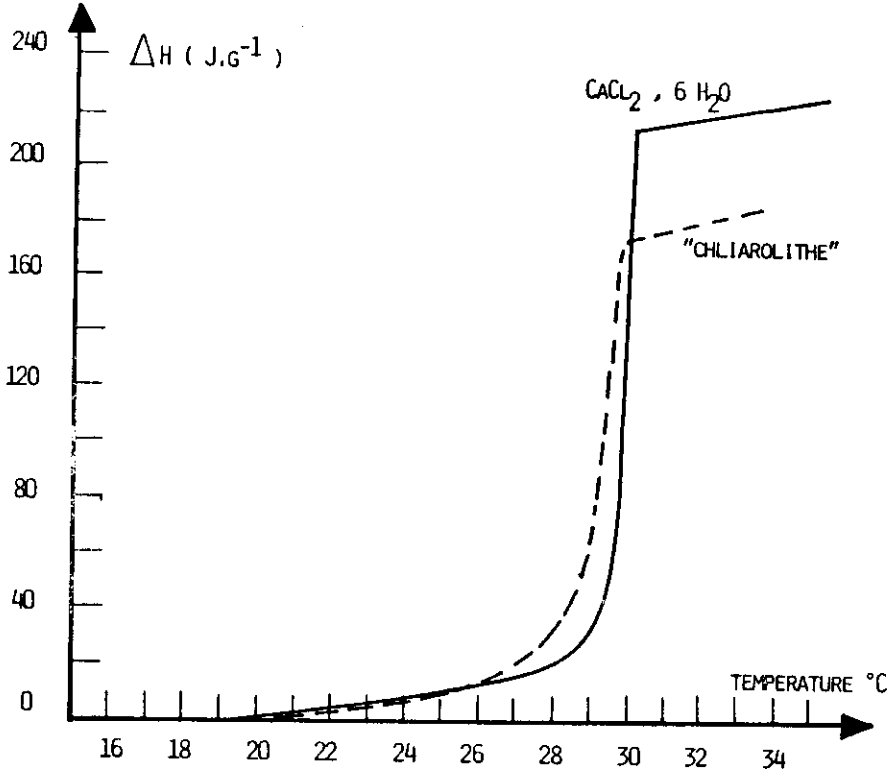


FIG. 6. COMPARED VARIATIONS OF LATENT HEAT OF MELTING FOR PURE CALCIUM CHLORIDE HEXAHYDRATE AND "CHLIAROLITHE", A MODIFIED CALCIUM CHLORIDE HEXAHYDRATE BY ADDING NUCLEATING AGENTS AND DIATOMITES AS THICKENER.

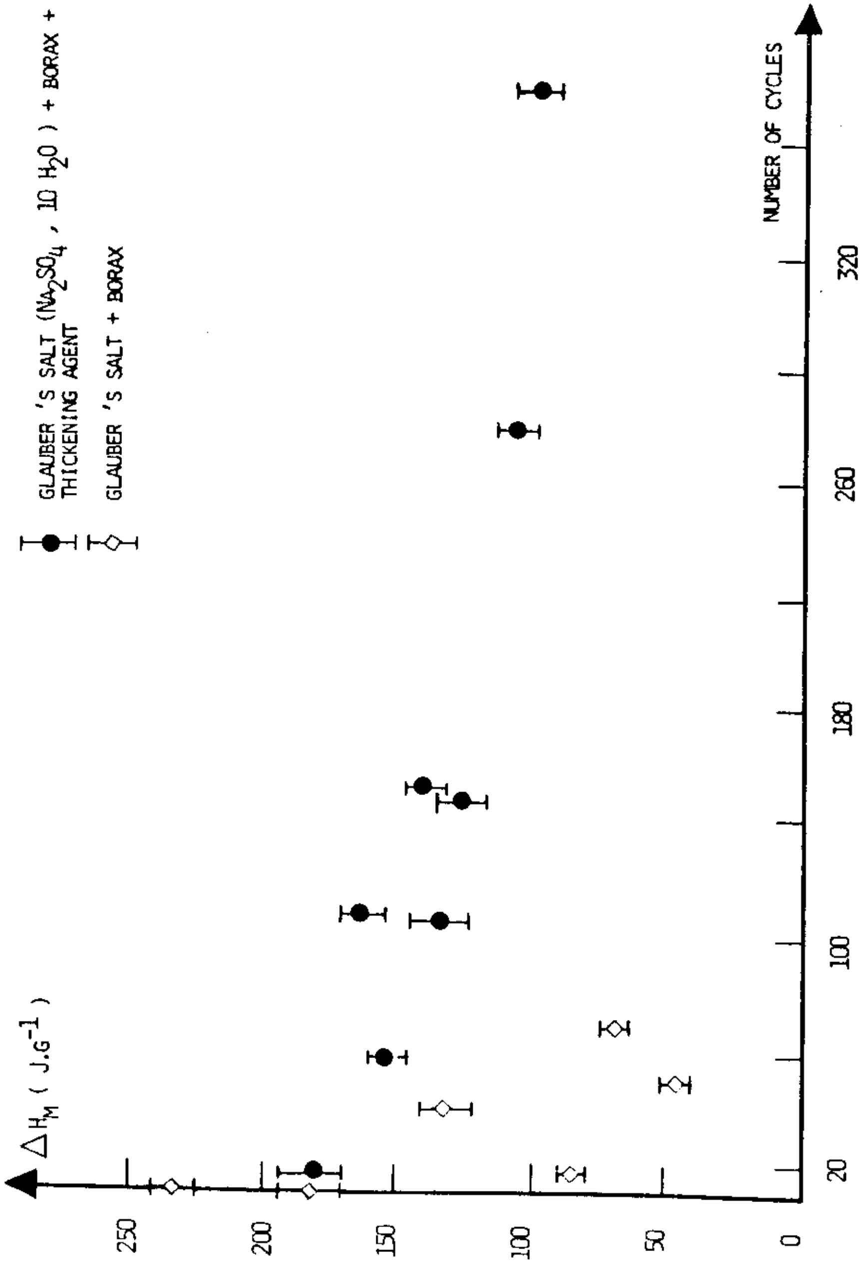


FIG. 3. DEGRADATION OF GLAUBER 'S SALT WITH CYCLING, FROM REF (31) .

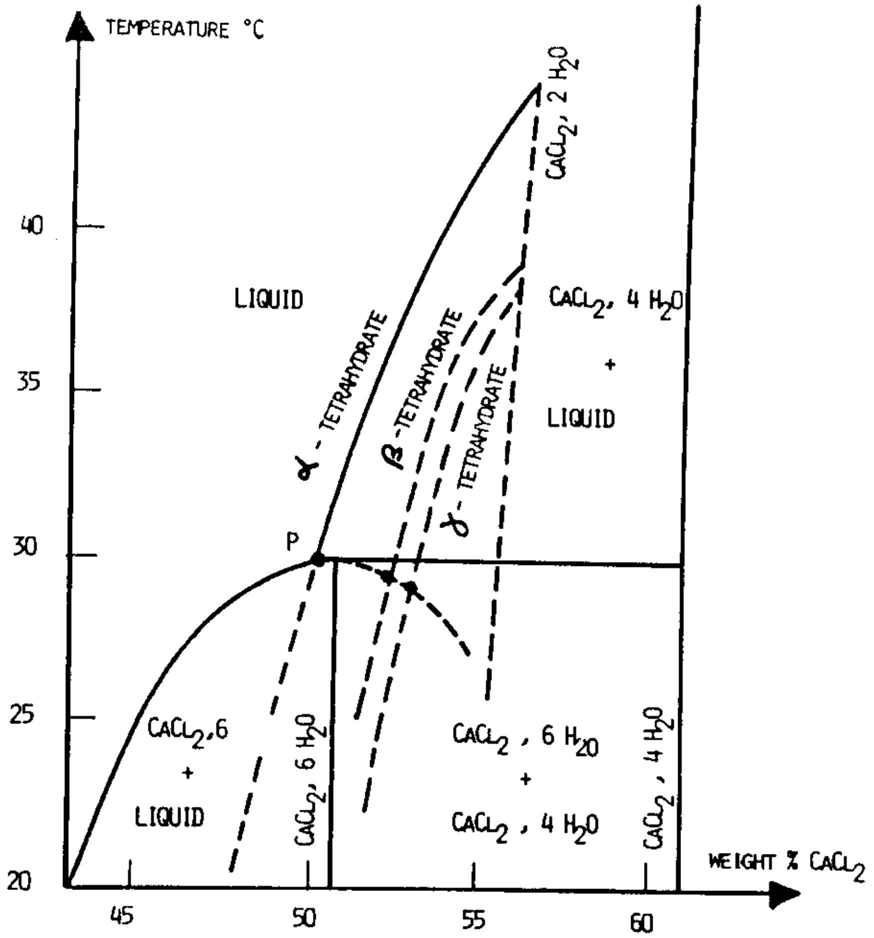


FIG. 4. PART OF THE PHASE DIAGRAM $CaCl_2 - H_2O$

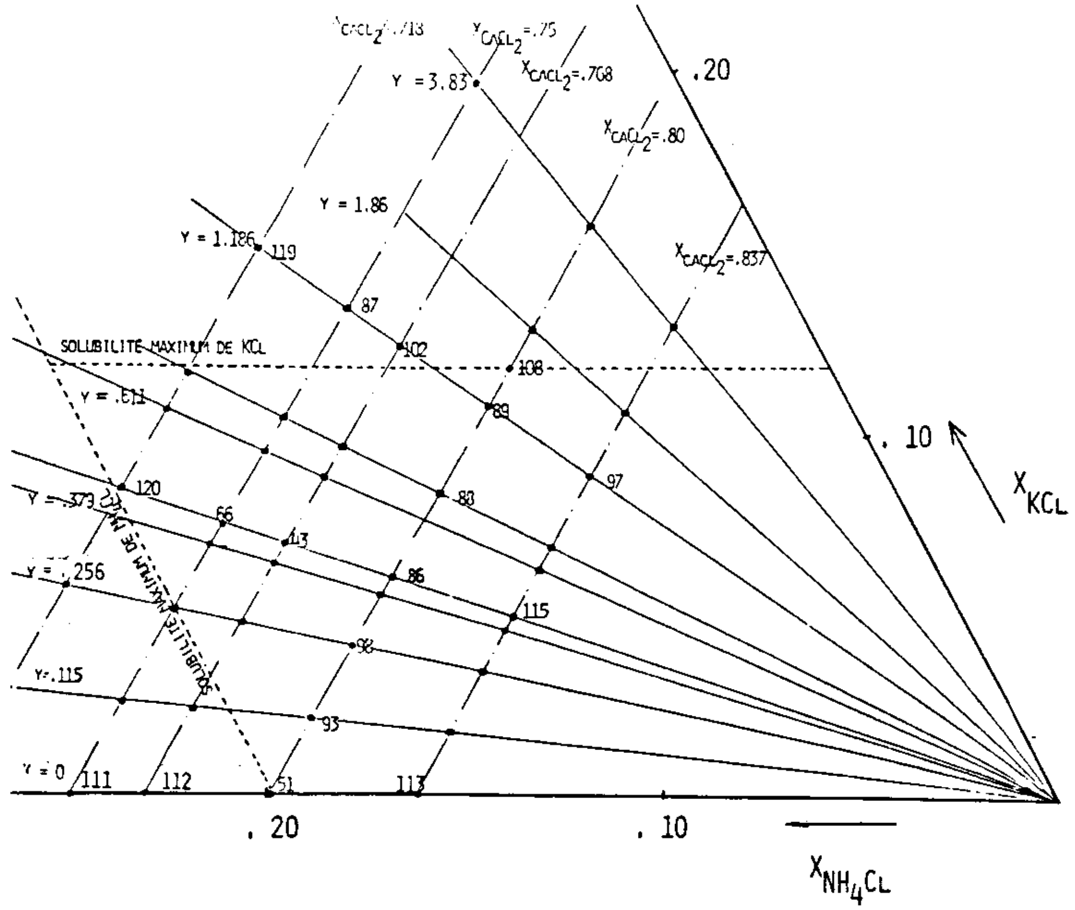

$X_{CACL_2}=.713$
$Y_{CACL_2}=.75$
$X_{CACL_2}=.768$
$X_{CACL_2}=.80$
$X_{CACL_2}=.837$
Y = 3.83
Y = 1.86
Y = 1.186
Y = .611
Y = .373
Y = .256
Y = .115
Y = 0
119
87
102
108
89
97
83
120
66
43
86
115
98
93
111
112
51
113
SOLUBILITE MAXIMUM DE KCL
SOLUBILITE MAXIMUM DE NACL
.20
.10
$X_{KCL}$
.20
.10
$X_{NH_4CL}$

FIG. 7

FIG. 8

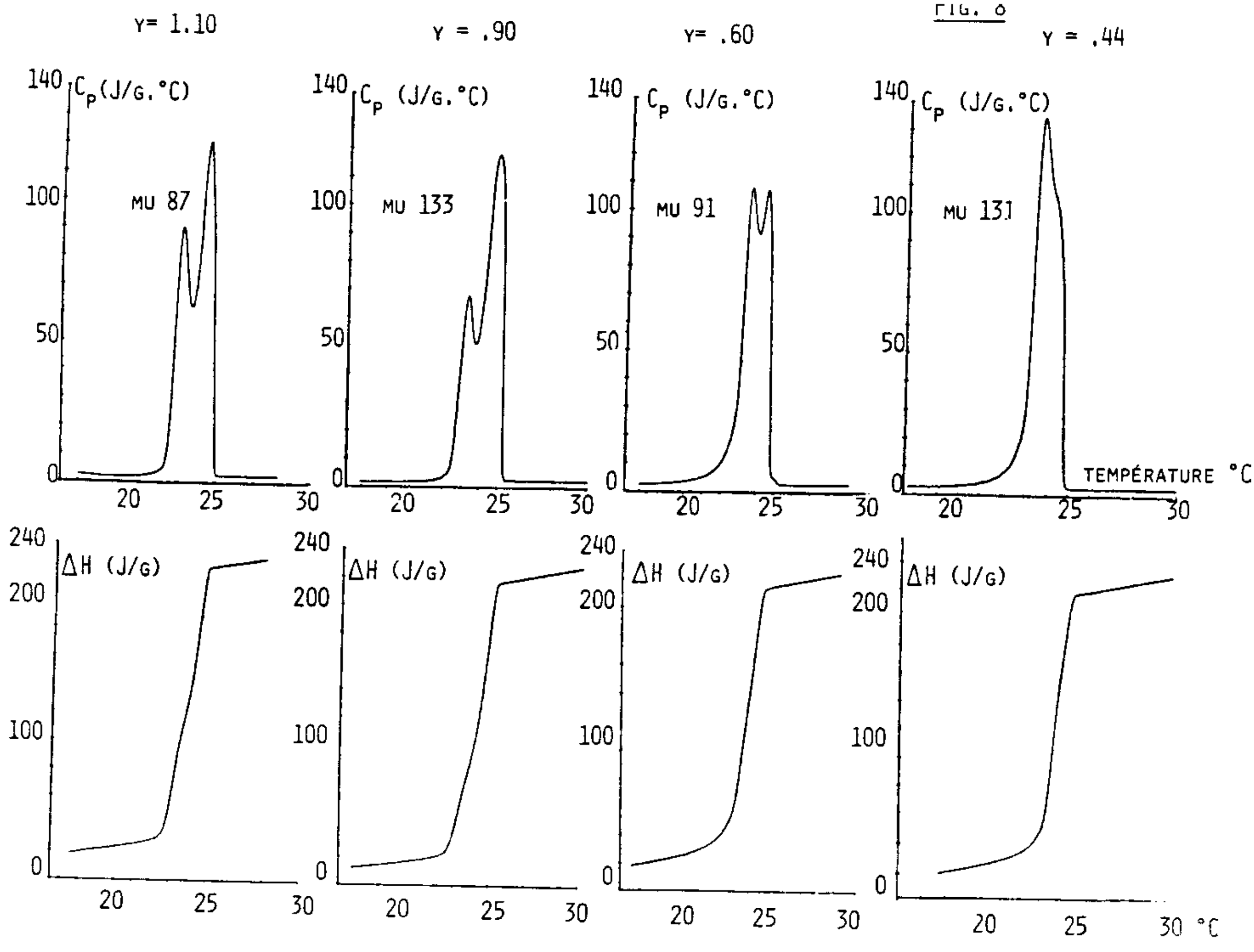

Y= 1.10
Y = .90
Y= .60
Y = .44
$C_P$ (J/G.°C)
140
100
50
0
MU 87
MU 133
MU 91
MU 131
TEMPÉRATURE °C
20
25
30
ΔH (J/G)
240
200
100
0
20
25
30 °C

FIG. 9

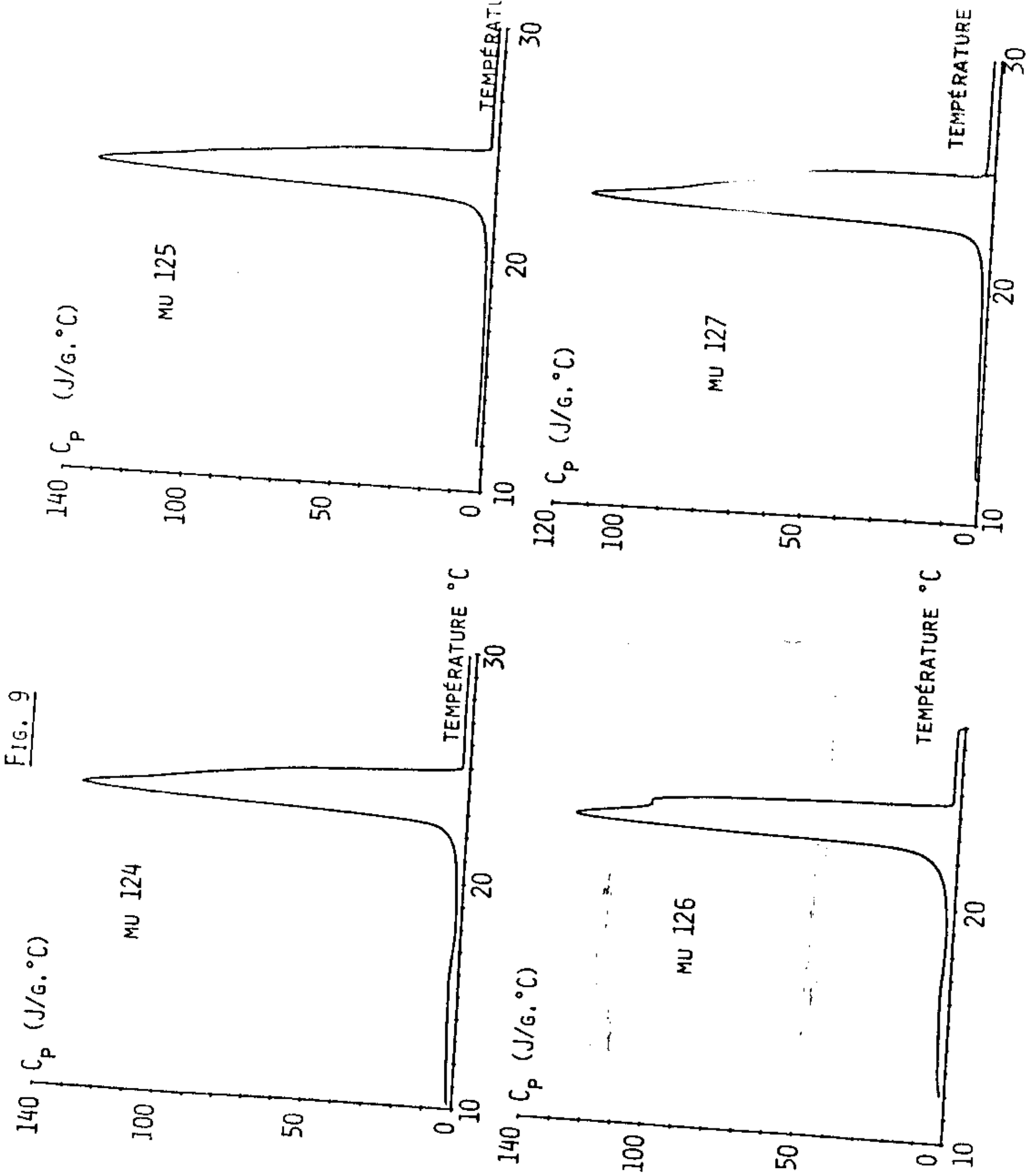

MU 125
MU 127
MU 124
MU 126
$C_p$ (J/G.°C)
TEMPÉRATURE °C
140
120
100
50
0
10
20
30

FIG 10.

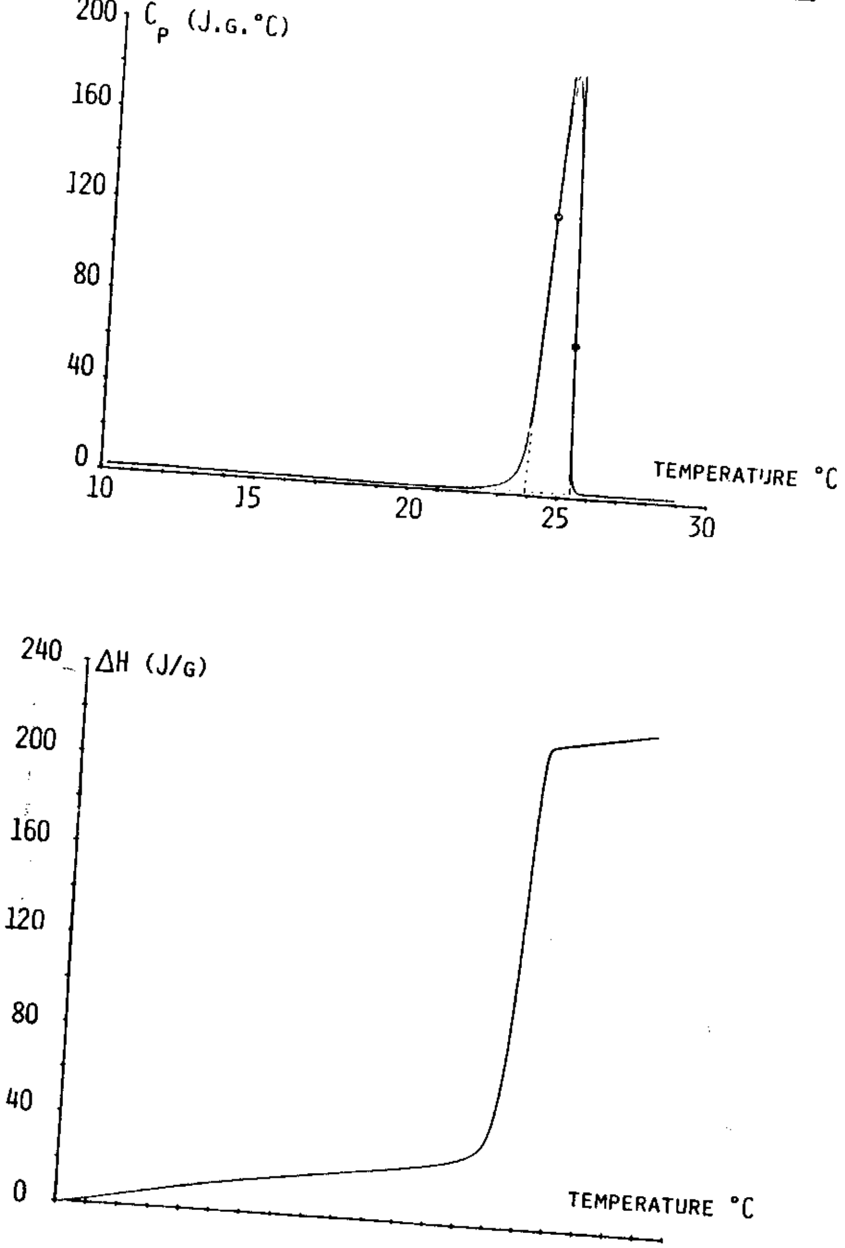

$C_p$ (J.G.°C)
200
160
120
80
40
0
10
15
20
25
30
TEMPERATURE °C
ΔH (J/G)
240
200
160
120
80
40
0
TEMPERATURE °C

FIG. 11

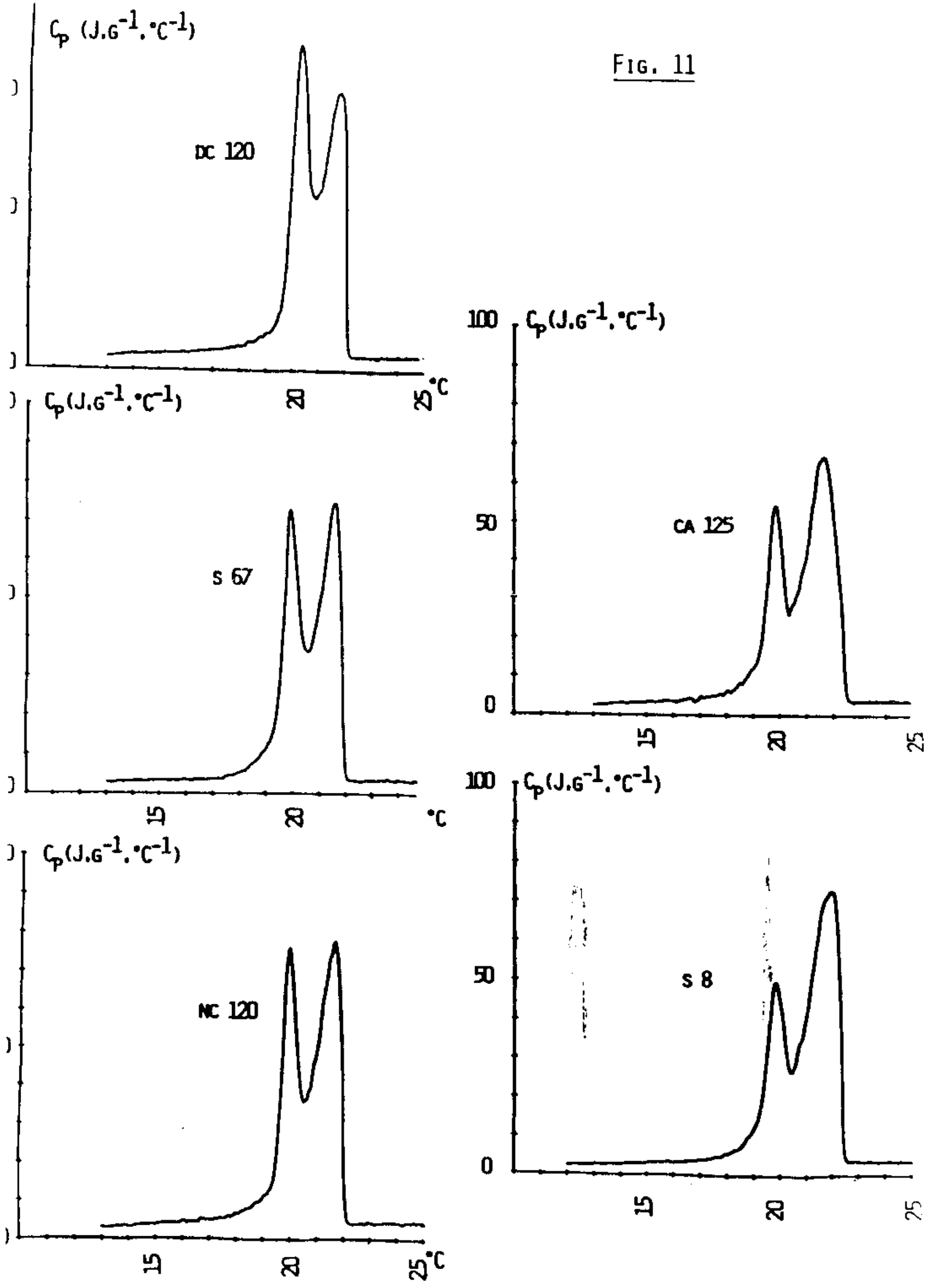

$C_p$ (J.G$^{-1}$.°C$^{-1}$)
DC 120
20
25
°C
$C_p$ (J.G$^{-1}$.°C$^{-1}$)
S 67
15
20
°C
$C_p$ (J.G$^{-1}$.°C$^{-1}$)
NC 120
15
20
25
°C
100
$C_p$ (J.G$^{-1}$.°C$^{-1}$)
50
CA 125
0
15
20
25
100
$C_p$ (J.G$^{-1}$.°C$^{-1}$)
50
S 8
0
15
20
25

FIG. 12

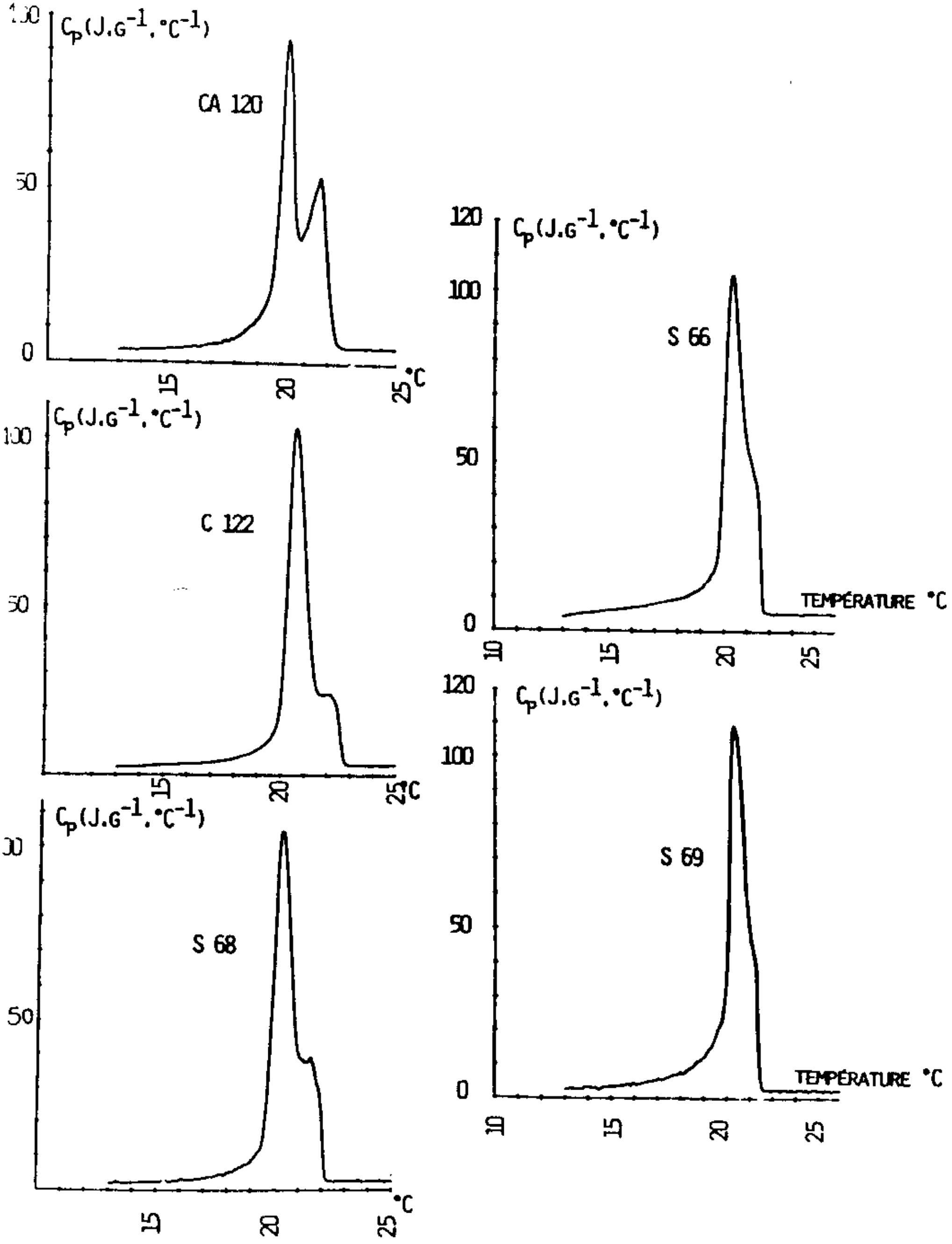

100
$C_p$ (J.G$^{-1}$.°C$^{-1}$)
CA 120
50
0
15
20
25
°C
$C_p$ (J.G$^{-1}$.°C$^{-1}$)
100
C 122
50
15
20
25
°C
$C_p$ (J.G$^{-1}$.°C$^{-1}$)
100
S 68
50
15
20
25
°C
120
$C_p$ (J.G$^{-1}$.°C$^{-1}$)
100
S 66
50
0
TEMPÉRATURE °C
10
15
20
25
120
$C_p$ (J.G$^{-1}$.°C$^{-1}$)
100
S 69
50
0
TEMPÉRATURE °C
10
15
20
25

FIG. 12

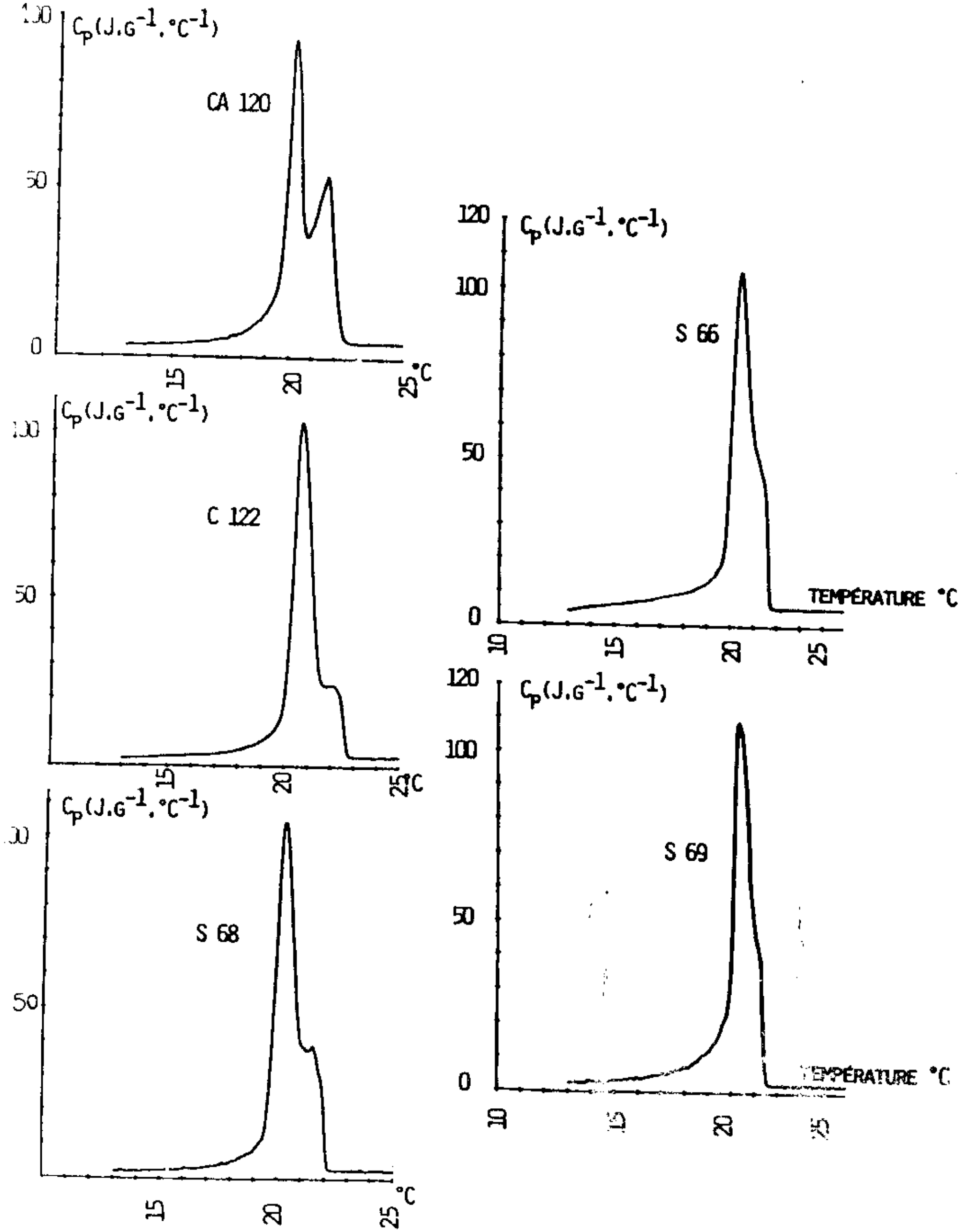

$C_p$ (J.G$^{-1}$.°C$^{-1}$)
CA 120
C 122
S 68
S 66
S 69
100
50
0
120
10
15
20
25 °C
TEMPÉRATURE °C

FIG. 13

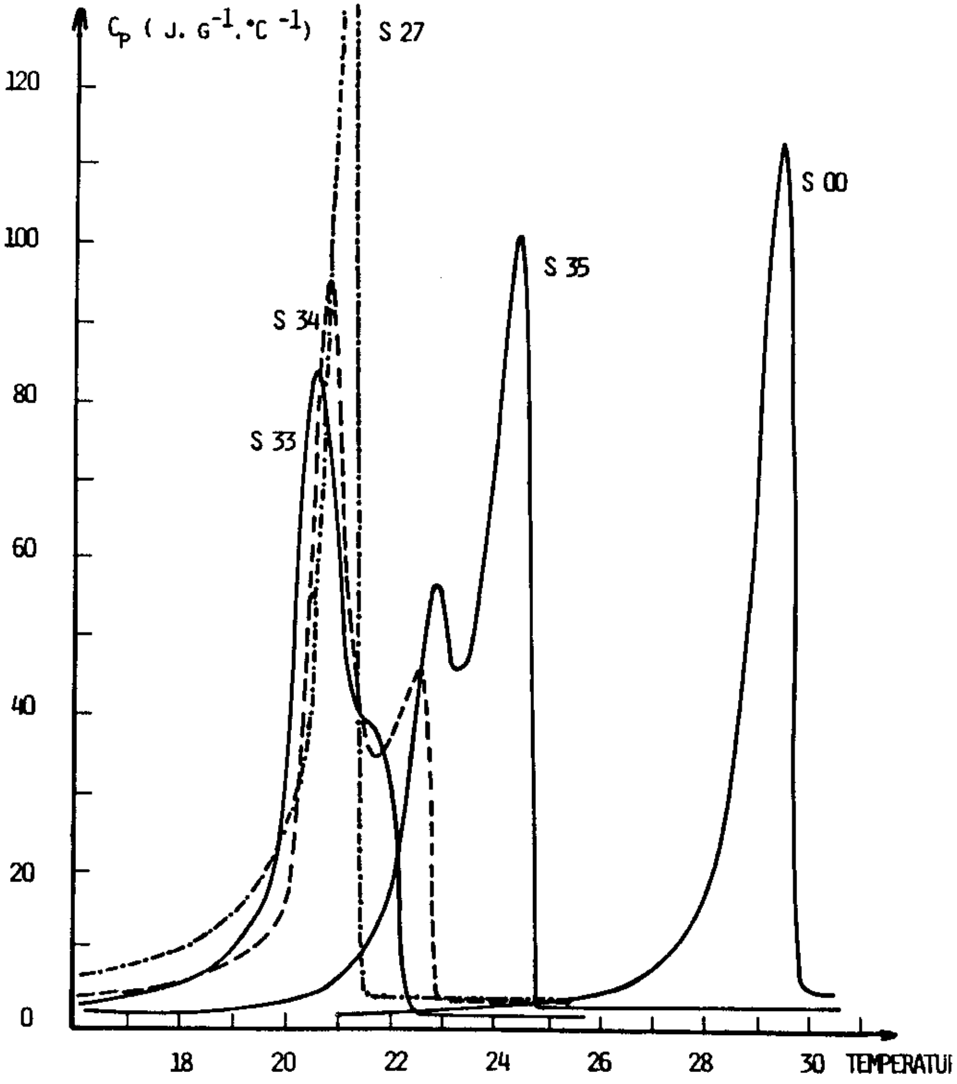
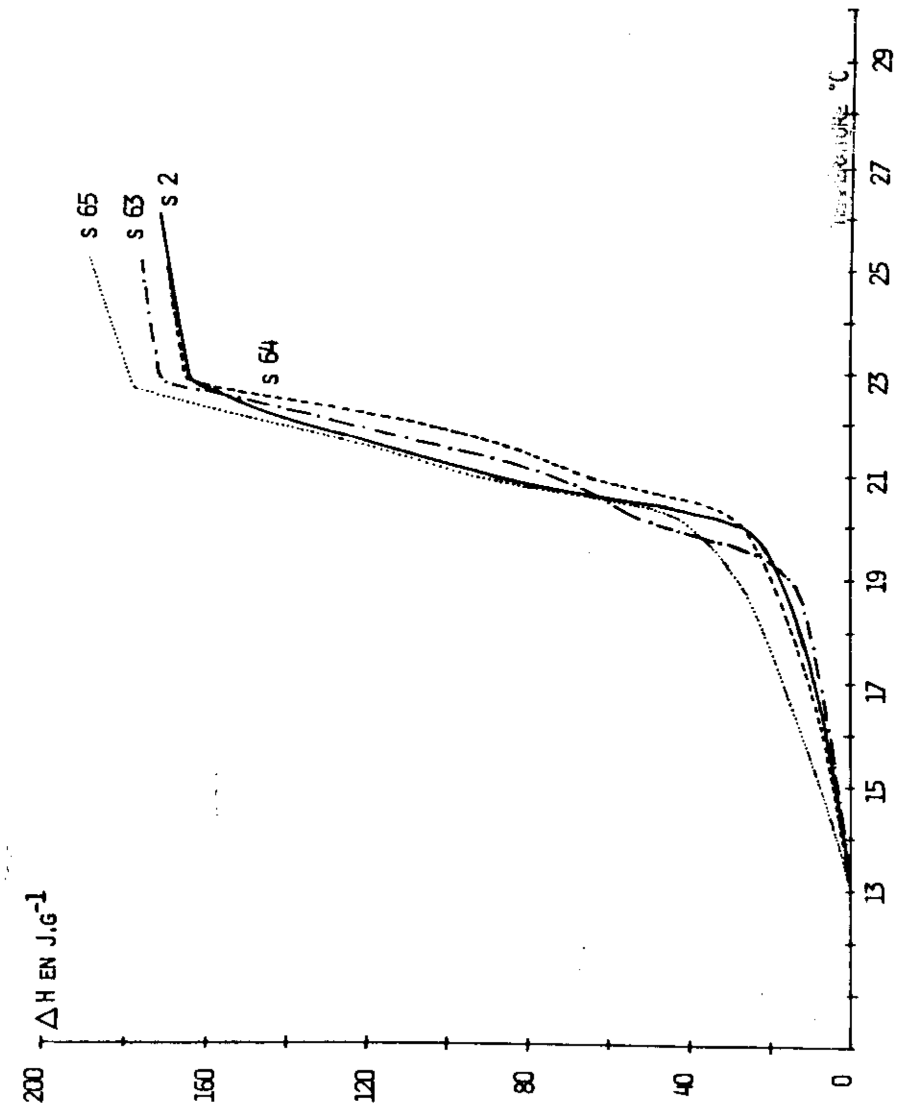

$C_p$ ( J. G$^{-1}$.°C $^{-1}$)
S 27
S 00
S 35
S 34
S 33
120
100
80
60
40
20
0
18
20
22
24
26
28
30
TEMPERATU

FIG. 14



Δ H EN J.G$^{-1}$
200
160
120
80
40
0
13
15
17
19
21
23
25
27
29
Température °C
S 65
S 63
S 2
S 64