Transition Temperatures of the Hydrates of Na₂SO₄, Na₂HPO₄, and KF as Fixed Points in Biomedical Thermometry

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The hydrate transition temperatures of $Na_2SO_4 \cdot 10H_2O$ to Na_2SO_4, $KF \cdot 2H_2O$ to KF, and $Na_2HPO_4 \cdot 7H_2O$ to $Na_2HPO_4 \cdot 2H_2O$ were established using ACS grade salts as 32.374 °C, 41.422 °C, and 48.222 °C, respectively. A simple and reliable procedure involving inexpensive materials was used to realize these transitions as temperature fixed points. Each transition temperature was attained within 30 minutes of hydrate initiation and remained constant to within ±0.002 °C for more than 10 hours if the mixture was stirred. The established transition temperatures were sensitive at the 0.001 °C level to the amount of impurities, so the materials used should be of the highest quality available.

These systems fill a gap in the existing spectrum of temperature standards and should be useful in biomedical laboratories for calibrating thermometers.

Key words: biomedical thermometry; disodium hydrogen phosphate; fixed point; hydration temperature; potassium fluoride; salt hydrate; sodium sulfate; temperature calibration; temperature standard; thermistor; thermometer; transition temperature.

1. Introduction

Researchers in biomedical laboratories have become increasingly aware of the importance of temperature measurements as they strive to improve the overall quality of their tests and medical procedures. Currently, biochemists and physiologists are studying the temperature dependence of enzyme [1] [5] and cellular [2] reactions, while in the clinic, hyperthermia is being examined as an adjuvant therapy in cancer treatment [3], hypothermia is being used to prolong cardiac surgery in infants [4], and cryogenic techniques are being studied for organ and tissue preservation [5].

At the same time, there have been dramatic developments in biomedical instrumentation that both require and provide greater accuracy in temperature measurement. For example, electronic digital thermometers equipped with a variety of specialized sensors [6] are now available which indicate temperature to a resolution of 0.01 °C. These new, sophisticated instruments are being used to automate many test procedures. Valid measurements with these devices, however, require precise temperature control and accurate temperature measurement.

The only way to maintain thermometer accuracy, as with any other measurement, is through careful and well-documented calibrations at periodic intervals [7]. The purpose of this paper is to present a series of transition temperatures between the hydrates of inorganic salts as fixed points which can be used to calibrate thermometers quickly, easily, and with sufficient accuracy for most experimental purposes, i.e., to about ± 0.01 °C [8]. These could be used in conjunction with existing temperature fixed points such as the ice point and the gallium melting point (National Bureau of Standards, SRM 1968) [9]. Many inorganic compounds form crystals in definite states of hydration. The phase transitions which occur when states of hydration change were suggested long ago as potential temperature fixed points [10]. Specifically, we report in this paper a detailed study of three hydrate transitions: (1) the anhydrous to decahydrate transition of sodium sulfate (Na_2SO_4), (2) the anhydrous to dihydrate transition of potassium fluoride (KF), and (3) the dihydrate to heptahydrate transition of disodium hydrogen phosphate (Na_2HPO_4). In addition, we present the results of a preliminary study which included three other salts ($FeCl_3$, $Zn(NO_3)_2$, $Na_2S_2O_3$).

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1.1 History of the method

The idea of using the transition temperatures between hydrates of salts as fixed points for the calibration of thermometers was first suggested by M. Jeannel in 1866 [11], but received little attention until T. W. Richards rediscovered it in 1898 [12]. Richards and J. B. Churchill investigated several salt hydrate systems in considerable detail [13]. Their research demonstrated that such systems provide stable and reproducible temperature fixed points [14-19].

Although Jeannel had proposed using sodium acetate trihydrate, Richards began his research with sodium sulfate decahydrate, Glauber's salt. In 1898, he reported in a preliminary paper that Glauber's salt melts at 32.378 °C [12]. Then, in 1902, Richards and R. C. Wells carefully established the transition temperature for the complete dehydration of sodium sulfate decahydrate as 32.383 ± 0.001 °C [13]. H. C. Dickinson and E. F. Mueller, working at the National Bureau of Standards in 1907, confirmed these results when they obtained a value of 32.384 ± 0.003 °C on the International Hydrogen Temperature Scale [14] for the sosium sulfate transition temperature. As a result of these researches, the sodium sulfate decahydrate transition temperature and the freezing point of water [15] were the most accurately determined temperature fixed points of the time.

In 1899, Richards and Churchill outlined a research program to investigate the transition temperatures of nine salts which preliminary studies had shown were potentially useful as fixed points [16]. During the following twenty years, Richards and his coworkers established the transition temperatures between the hydrates of seven of those salts [17-21]. In addition to Richards, several other researchers have considered using salt hydrate transitions as fixed points in thermometry [22-24]. In 1930, H. O. Redlich and G. Loffler-Wein studied the transition temperatures of some ternary systems composed of two different salts and water using a platinum resistance thermometer [25]. In 1938, E. R. Washburn and W. J. Clem also used a platinum resistance thermometer to measure the metastable sodium sulfate heptahydrate to anhydrous salt transition temperature as 23.465 ± 0.004 °C [26]. These latter investigators all used the sodium sulfate decahydrate transition temperature to standardize their thermometers. Since 1938, a few papers have appeared concerning the use of salt hydrate transition temperatures as fixed points [27-30], but these are concerned only with attempts to use the sodium sulfate system and contribute little new information.

A list of the established salt hydrate transition systems with the reported transition temperatures is given in table 1. Although these systems cover the temperature range from 10 to 90 °C fairly well, there are some sizable gaps. Of particular significance to biomedical researchers is the gap from 35.36 to 50.664 °C. A literature search for salt hydrate

TABLE 1. *Temperature fixed points established using transitions between different states of hydration of salts.*

	Hydrate Transition	Transition Temperature (°C)		
Salt	States of Hydration	As Reported	On IPTS-68	Ref.
Na_2CrO_4	$10H_2O-6H_2O$	19.529	19.522	19
Na_2CrO_4	$10H_2O-4H_2O$	19.987	19.980	19
Na_2SO_4	$7H_2O-0H_2O$	23.465	23.457	26
Na_2CO_3	$10H_2O-7H_2O$	32.017	32.008	24
Na_2SO_4	$10H_2O-0H_2O$	32.383	32.373	12,13,14
Na_2CO_3	$10H_2O-1H_2O$	32.96	32.95	20
Na_2CO_3	$7H_2O-1H_2O$	35.37	35.36	20
NaBr	$2H_2O-0H_2O$	50.674	50.664	17
$MnCl_2$	$4H_2O-2H_2O$	58.089	58.079	18
$SrCl_2$	$6H_2O-2H_2O$	61.341	61.331	21
$SrBr_2$	$6H_2O-2H_2O$	88.62	88.62	21

TABLE 2. *Transitions potentially useful as fixed points.*

	Hydrate Transition	Transition Temperature	
Salt	States of Hydration	Reported (°C)	Ref.
$Ba(C_2H_3O_2)_2$	$3H_2O-1H_2O$	24.7	31
Na_2SeO_4	$10H_2O-0H_2O$	32	38
Na_2HPO_4	$12H_2O-7H_2O$	35.0, 35.2	32,33
$Zn(NO_3)_2$	$6H_2O$ congruent	36.1	34
$Ba(C_2H_3O_2)_2$	$1H_2O-0H_2O$	41	31
KF	$2H_2O-0H_2O$	41	35
$Na_2S_2O_3$	$5H_2O-2H_2O$	48.17	36,37
Na_2HPO_4	$7H_2O-2H_2O$	40.0, 48.3	32,33
Na_3PO_4	$12H_2O-$unknown	73.5	16
$Ba(OH)_2$	$8H_2O-$unknown	78.0	16
Na_2HPO_4	$2H_2O-0H_2O$	95.2, 95	32,33

transitions has produced the supplemental list shown in table 2 [31-38]. These systems were considered to have potential as temperature fixed points to fill the gaps in table 1.

2. Experimental method

2.1 Salt transitions

The hydrated crystal is a distinct phase of the water : salt binary system. The phase transition which occurs when a hydrated inorganic salt changes its state of hydration may be either congruent or incongruent depending on whether one or two solid phases are involved. In the former, the hydrated salt forms a saturated solution of the same composition. The liquid, solid and vapor phases ($P=3$) all have the same composition. Hence, the system may be considered to have but one component ($C=1$). In this instance, the Phase Rule [39], $F = C - P + 2$, predicts that the number of degrees of freedom (F) will vanish and a triple point will result. This is an unrealistic situation, of course, because it requires the salt to have the same vapor pressure as water at

the transition temperature in order for the vapor phase composition to be the same as that of the solid phase. Furthermore, if the starting material deviates from the crystal stoichiometry, the composition of the solution will change as the transition progresses, and with it, the temperature. This behavior can be understood by considering the phase diagram for the system $Zn(NO_3)_2 : H_2O$ shown in figure 1 [34]. If a solution with composition 63.6 percent $Zn(NO_3)_2$ by weight is cooled from 40 °C, the hexahydrate will form, the composition of the solution will remain unchanged, and the temperature will remain at 36.1 °C during the entire hydration process. Thus, the phase transition is congruent and simulates the liquid-solid transition of a single pure material. If a solution of composition 60 percent $Zn(NO_3)_2$ by weight is cooled from 40 °C, however, it will not start forming the hexahydrate until the temperature is below 34 °C. Once crystallization starts, the solution becomes more dilute and the transition temperature decreases. Thus, a congruent transition is very sensitive to composition.

By contrast, a salt undergoing an incongruent transition exhibits four phases: liquid, vapor, and two solids in different states of hydration. In this case, the Phase Rule unequivocally predicts a quadruple point with zero degrees of freedom for the two component system. The presence of four phases lends a degree of compositional stability to the quadruple point as long as the system is sufficiently rich in salt to keep the solution saturated at the transition. This situation is illustrated by the phase diagram for $Na_2SO_4 : H_2O$ shown in figure 2 [40]. In this case, any mixture of salt and solution with a total composition of 33.2 percent or more Na_2SO_4 cooled from 40 °C will start to form crystalline decahydrate at about 32.4 °C and will remain at that temperature until either the water (if the Na_2SO_4 composition is greater than 44.1 percent) or the anhydrous phase is exhausted.

As shown in figure 3, the system $Na_2HPO_4 : H_2O$ exhibits two incongruent transitions [32,33,40]: one at about 48 °C from the heptahydrate to the dihydrate, and the other at about 35 °C from the dodecahydrate to the heptahydrate. At each of these transitions, the behavior of this system should be similar to that of sodium sulfate. It is possible for a single system to have both congruent and incongruent transitions, as illustrated by the phase diagram for $KF : H_2O$ shown in figure 4 [35,40].

Two additional salt : water systems were surveyed: (1) the $FeCl_3 : H_2O$ system, which has a phase diagram [40] qualitatively similar to that for $Zn(NO_3)_2 : H_2O$, and (2) the sodium thiosulfate system, $Na_2S_2O_3 : H_2O$, which has a very complex phase diagram [36,37,40] with several metastable phases in a small temperature range about 48 °C.

The six systems investigated are listed in table 3 along with the number of tests conducted on each salt and with the type of transition observed.
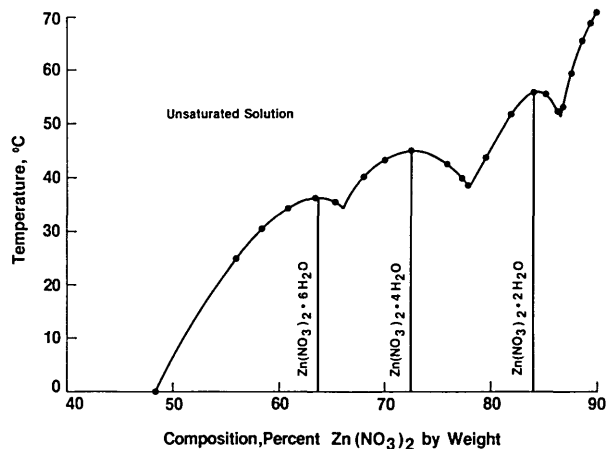

FIGURE 1. Phase diagram for the system $Zn(NO_3)_2 : H_2O$. The melting points of the dihydrate, tetrahydrate, and hexahydrate are all congruent.
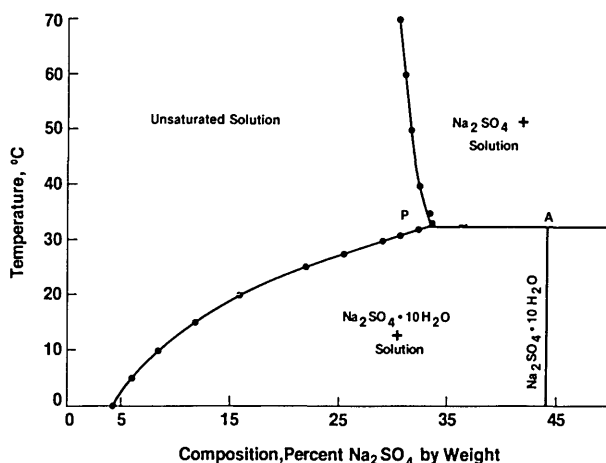

FIGURE 2. Phase diagram for the system $Na_2SO_4 : H_2O$. The melting point of the decahydrate is incongruent.

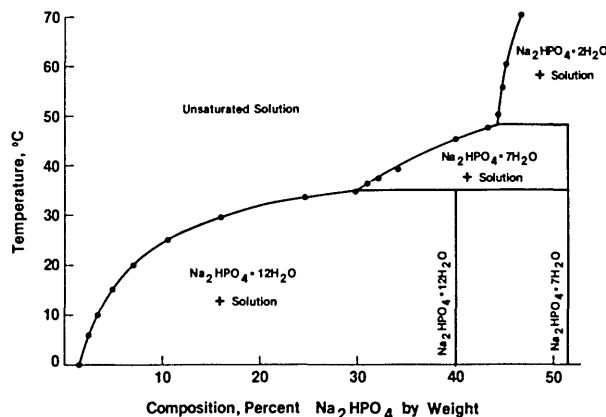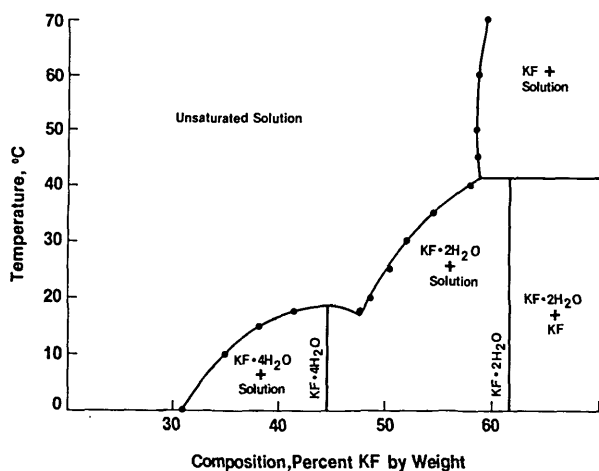FIGURE 3. Phase diagram for the system $Na_2HPO_4 : H_2O$.

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FIGURE 4. Phase diagram for the system KF:H₂O.

TABLE 3. *Salt systems examined in this report.*

Salt Hydrate	Transition Temperature (°C)	Transition Type	Number of Tests
Na₂SO₄·10H₂O	32.4	incongruent	19
Zn(NO₃)₂·6H₂O	36	congruent	5
FeCl₃·9H₂O	37	congruent	3
KF·2H₂O	41.4	incongruent	20
Na₂S₂O₃·5H₂O	48.2	incongruent	6
Na₂HPO₄·7H₂O	48.2	incongruent	18

2.2 Salt samples

Analytical grade samples of each of the salts just discussed were obtained in 454 gram quantities from commercial (J. T. Baker, Fisher, Mallinckrodt) sources. In most cases, the samples came in glass bottles with lot number and lot analysis (or maximum impurity levels) on the bottle label. The KF·2H₂O samples were received in plastic bottles. Except for a few samples of sodium sulfate, all samples were obtained in crystalline form and were the highest purity grade available from each supplier. In table 4, the manufacturer's analysis of each lot studied is presented.

2.3 Thermometry

The temperature measuring apparatus used in this experiment employed six very stable and well-aged thermistors as sensing elements. The thermistors were connected in a series circuit with a constant current source and a thermostated, precision, ten kiloohm resistor as shown schematically in figure 5. The resistance of each thermistor was determined in terms of the resistance of the precision "standard" resistor by measuring the potential differences

TABLE 4. *Impurity analysis, supplied by manufacturer, of each lot used in the determination of the transition temperatures.*

Na₂SO₄·10H₂O	Lot Number			
Contaminant (ppm)	092	558	026	824*
Insoluble Matter	20	20	50	—
Chloride	5	3	3	—
Calcium, Magnesium	20	30	40	—
Phosphate	—	5	4	—
Free Acid (as H₂SO₄)	—	20	50	—
Free Alkali	—	none	none	—
Nitrogen Compounds (as N)	3	2	5	—
Arsenic	0.5	0.1	0.1	—
Heavy Metals (as Pb)	2	2	5	—
Iron	<3	2	3	—

KF·2H₂O				
Contaminant (ppm)	165	498	533	644
Iron	10	2	10	10
Chloride	10	10	50	50
Sulfate	30	10	50	50
Sulfite	50	50	—	—
Free Acid (as HF)	1000	40	500	500
Heavy Metals (as Pb)	10	5	30	30
Insoluble Matter	20	50	200	200
Free Alkali (as K₂CO₃)	none	none	1000	1000
Silicofluoride (K₂SiF₆)	100	60	500	500
Sodium	—	—	200	200

Na₂HPO₄·7H₂O				
Contaminant (ppm)	150	149	478	876
Insoluble Matter	5	30	50	50
Chloride	<5	10	10	10
Sulfate	<20	20	50	50
Heavy Metals (as Pb)	<5	<5	10	10
Iron	5	<5	10	10
Nitrogen Compounds (as N)	3	3	10	10
Arsenic	2	5	5	5

*Technical grade

across the thermistor (V_t) and the "standard" (V_s) in the sequence: $V_t, V_s, -V_s, -V_t$. The measuring current was $10 \,\mu A$ in all measurements and calibrations. The potential differences were measured with a precision digital voltmeter (DVM) which had an input impedance in excess of $10^9 \,\Omega$ and a sensitivity of 10^{-7} V on the lowest scale. Five digits were displayed with a 160 percent overrange capability, so that the least-count resolution of the system in terms of temperature was about a quarter of a millidegree Celsius (m°C). The thermometer circuit was controlled by a minicomputer operating through an instrument bus so that the selection of sensors, thermistor current, and reading rates could be preprogrammed. The data were logged onto a magnetic disc at predetermined intervals during each experiment and later plotted as time-temperature profiles.

The thermistors were calibrated against a Standard Platinum Resistance Thermometer (SPRT) whose resistance was
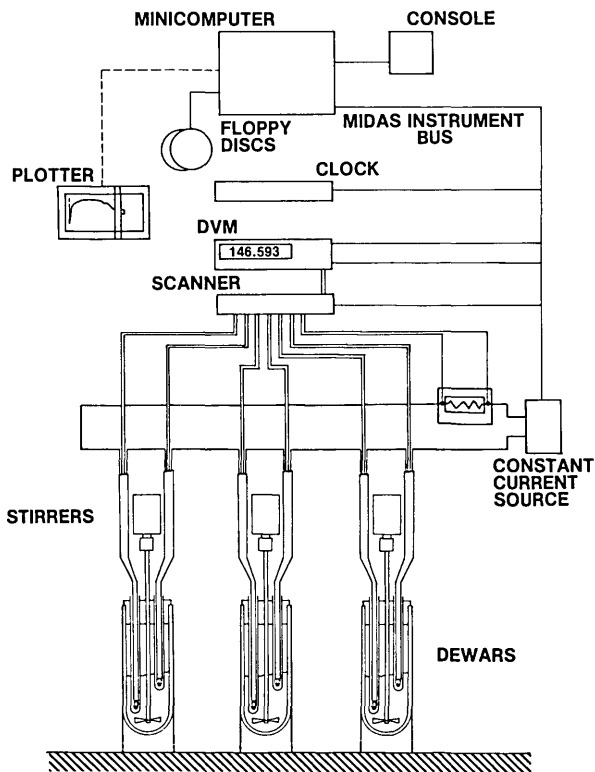
FIGURE 5. Temperature measurement system.

FIGURE 6. Schematic of experimental apparatus showing placement of thermistor temperature sensor and stirring propeller in 665 mL dewar.

measured with a Cutkosky AC Resistance Bridge [41]. The calibration was done with thermistors and SPRT inserted into a copper block immersed in a well-stirred constant temperature bath. The temperature of the copper block was kept constant to within a few tenths of a millidegree Celsius. When the calibration data were fitted to a modified Steinhart equation [42], the largest deviation was one-half of a millidegree Celsius. The uncertainty in realizing IPTS–68 temperatures by the SPRT, in terms of the scale as maintained at NBS, was no more than $\pm$ 0.001 °C. The uncertainty in the thermistor measurements was about $\pm$ 0.001 °C as a result of (a) calibration, $\pm$ 0.0005 °C; (b) drift of thermistors between calibrations, $\pm$ 0.0002 °C; (c) limiting precision of the measurement, $\pm$ 0.0002 °C; and (d) possible variations in the self-heating of thermistors during measurement, $\pm$ 0.0001 °C. Thus, the overall uncertainty in the temperatures is $\pm$ 0.002 °C.

2.4 Apparatus

A diagram of the apparatus used for the transition temperature determinations is shown in figure 6. During the measurements, the salt hydrate mixture was contained in a 665 mL glass dewar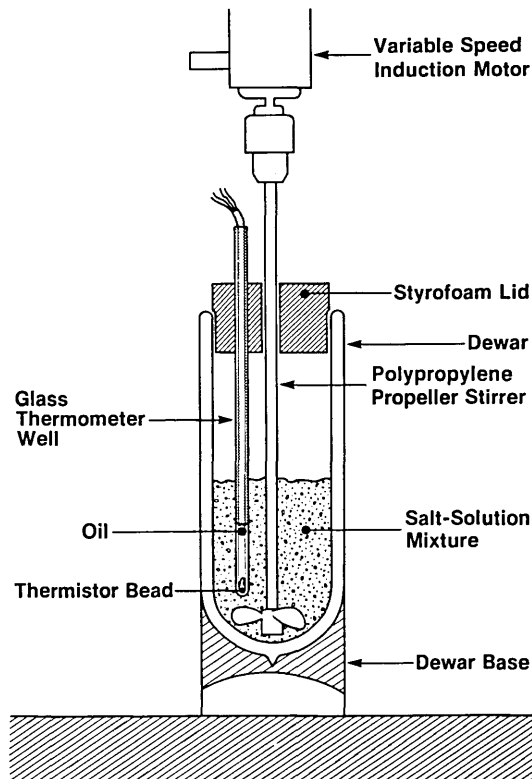 covered by a styrofoam lid through which holes were drilled to accommodate a polypropylene propeller stirrer and glass thermometer wells. Normally, two thermistors in glass wells were used to measure the temperature of the mixture, one located 1 cm below the surface of the liquid and the other positioned 0.5 cm above the stirrer blades (3.5 cm below the surface of the liquid). The stirrer was driven at slow speed (200 rpm) by an induction motor with a variable speed drive attachment. Commutating motors could not be used as the electrical noise generated by the commutators affected the voltmeter readings.

A smaller, styrofoam-insulated beaker apparatus was used in a series of preliminary experiments. That apparatus consisted of a glass beaker (250 or 400 mL), plastic acrylic lid, and paired high density styrofoam sides (2 to 4 cm thick). The stirring method and the arrangement of glass thermistor wells were the same as that used in the dewar apparatus, except that commutating motors were used in these experiments.

2.5 Procedures

The transition temperature of each sample was determined in the following manner. The dewar, propeller stirrer, and glass wells were cleaned in tap water, rinsed with distilled

water, and soaked overnight in a dilute solution of HCl. Following the acid soak, the components were rinsed thoroughly with distilled water and allowed to drain. Bottles containing 454 g of a hydrated salt were partially immersed in a water bath whose temperature was approximately ten degrees Celsius above the transition temperature. Within one to two hours, the hydrated salt lost its waters of hydration, leaving a fine powder of the anhydrous salt (or lower hydrate) settled out of the solution. Occasionally, while the hydrated salt was being heated, the less hydrated form would crystallize in a hard mass on the bottom of the bottle, and it was necessary to break up this mass by very vigorous shaking. The water bath containing the bottle of the salt: Solution mixture was allowed to cool to a few degrees Celsius below the transition temperature. The hydration process was initiated when the bottle was removed from the bath and shaken. Normally this procedure would result in the onset of crystallization which could be detected by observing the sudden appearance of solid on the walls of the bottle. At this point, the bottle was opened and the contents poured into the dewar. The amount of residual salt remaining in the bottle was between five and ten grams.

On the few occasions when the transferred mixture had not begun to crystallize, the transition was initiated by adding a small quantity (1 to 5 g) of powdered hydrated crystals. When it was necessary to take this approach, we found that using finely powdered crystals generally resulted in a more rapid recalescence and a flatter plateau than did a few large crystals. As soon as the hydrating salt mixture was in the dewar, the thermometers and stirrer were inserted, the lid assembled and the stirrer started. The transition temperature was then monitored continuously for the next 15 to 30 hours.

An additional set of experiments investigated the characteristics of the sodium sulfate decahydrate transition under various conditions. In several of these experiments, the samples were prepared and solidified in 250 mL or 400 mL glass beakers, or in 265 mL dewars. Samples of 250 g or *ca.* 350–420 g were prepared by either driving off the waters of hydration, as described above, or by combining distilled water with anhydrous salt in the same proportion as that in the hydrated salt. In both cases, the mixture was brought to equilibrium several degrees Celsius above the transition temperature before cooling. After the mixture had supercooled about 0.3 °C below the transition temperature, the transition was initiated by adding 0.1 to 10 g of finely ground crystals of the appropriate hydrated salt.

3. Results

3.1 Preliminary survey

The six hydrated salts considered in the initial survey are listed in table 3. On the basis of the survey results, three of the salt systems were not considered further in this study. The hydration transitions of the ferric chloride system, $FeCl_3 : H_2O$, were difficult to initiate. Once the transition was started, the temperature did not maintain a plateau and displayed fluctuations of ± 0.03 °C. Although sodium thiosulfate at first appeared stable, during subsequent trials the temperature displayed sharp, random changes of order 0.01 °C. Also, the measured values of the transition temperatures from different trials varied by as much as ± 0.1 °C. This behavior may reflect the presence of several metastable phases, as indicated by its phase diagram [36]. It was difficult to initiate the formation of zinc nitrate hexahydrate, although once started, the transition temperature appeared quite stable. Further difficulty in working with this system was encountered when lots labelled hexahydrate exhibited transitions at about 42 °C, indicating that the samples were of composition closer to that of the tetrahydrate (see fig. 1). Each of the three remaining salts appeared to exhibit sufficient stability and reproducibility to merit a more thorough examination.

During the preliminary experiments, a hydrated salt was sometimes reheated and the transition temperature measurements repeated. In these cases, the plateau temperatures determined were between 2 and 10 m°C less than the initial value. Because of this plateau temperature depression, probably due to contamination introduced during the first rehydration, only single runs on each hydrated salt were used for the principal temperature determinations.

3.2 Principal temperature determinations

In the principal set of experiments, time-temperature profiles were made of the hydration transitions of 57 samples of the three salts $Na_2SO_4 \cdot 10H_2O$, $KF \cdot 2H_2O$, and $Na_2HPO_4 \cdot 7H_2O$. The transitions were studied by monitoring the temperatures of the hydrating samples following the general procedure outlined above.

A typical time-temperature profile for each salt is shown in figure 7. The maximum temperature sustained during the "plateau period" was taken as the plateau temperature. The average plateau temperature, the number of samples, and the standard deviation of the temperatures for each lot are presented in table 5.

Both table 5 and figure 7 point out the substantial differences in behavior between the three salts. The sodium sulfate decahydrate was by far the most consistent. Nearly every profile was almost identical to that shown in figure 7. The recalescence period was so short that the sample temperature was within 0.002 °C of the plateau temperature in less than 15 minutes from the start of the transition. In the few instances in which the temperature of the mixture was not constant at the plateau temperature, it decreased by less than 0.002 °C in 20 hours.
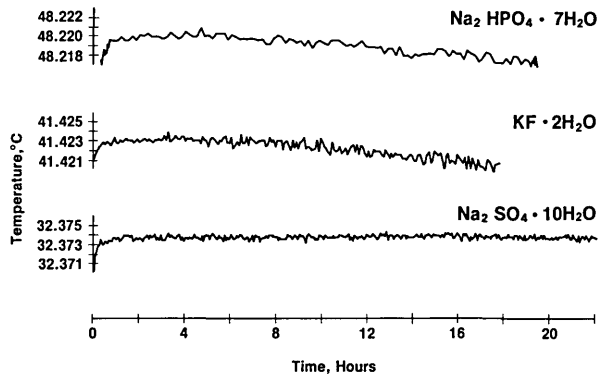
FIGURE 7. Typical temperature versus time profiles for the three reported salt transitions. Each transition was initiated at zero hours and the mixture stirred continuously.

TABLE 5. *Results of principal temperature determinations, summarized by salt and lot.*

Salt Hydrate	Lot	Number of Samples	Average Plateau Temperature (°C)	Standard Deviation (°C)
$Na_2SO_4 \cdot 10H_2O$				
	092	7	32.373_0	0.000_6
	558	3	32.373_2	0.000_8
	026	3	32.373_3	0.000_7
	824	6	32.373_8	0.001_1
$KF \cdot 2H_2O$				
	165	5	41.393_8	0.001_4
	498	8	41.421_5	0.001_7
	533	6	41.383_5	0.001_0
	644	1	41.410	—
$Na_2HPO_4 \cdot 7H_2O$				
	150	4	48.215_5	0.002_3
	149	8	48.216_5	0.004_2
	478	3	48.216_1	0.003_0
	876	3	48.221_7	0.005_1

The shape of the time-temperature profile for $KF \cdot 2H_2O$ was nearly as reproducible as that for sodium sulfate, i.e., it displayed a rapid recalescence followed by a gradual change in the temperature of less than 0.002 °C over the next 20 hours. As can be seen from the data in table 5, however, the measured plateau temperatures varied considerably from lot to lot.

The most variable behavior within a lot was recorded for $Na_2HPO_4 \cdot 7H_2O$. The shapes of these profiles ranged from the eighteen hour plateau shown in figure 7 to those that remained constant for only a few hours before rapidly decreasing at up to 0.005 °C/h. With the exception of one contaminated lot which has not been included, however, the temperature of hydration changed by less than 0.010 °C over a period of at least 20 hours.

3.3 Immersion studies

In order to determine the best value for the hydration temperature of each salt, it was necessary to ascertain the effects of thermometer immersion into the stirred salt : solution mixture. Several experiments were conducted in which two or three thermometers were immersed to different depths in the mixtures. Figures 8, 9, and 10 show results for each salt which indicate an apparent top to bottom temperature gradient within the hydrating mixture of approximately 5 m°C. In addition, a single thermistor was used to probe vertically a $Na_2HPO_4 : H_2O$ mixture two hours after the transition had been initiated. The mixture was probed at three radial positions, 0.9 cm, 1.8 cm, and 2.7 cm, from
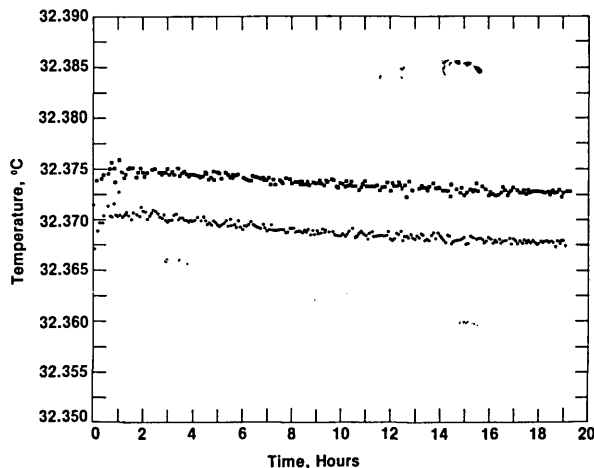

FIGURE 8. Temperature versus time profiles for the $Na_2SO_4 \cdot 10H_2O$ transition recorded at 3.5 cm (■) and 1.0 cm (●) below the surface of the mixture. The stirring propeller was located 4.0 cm below the surface.
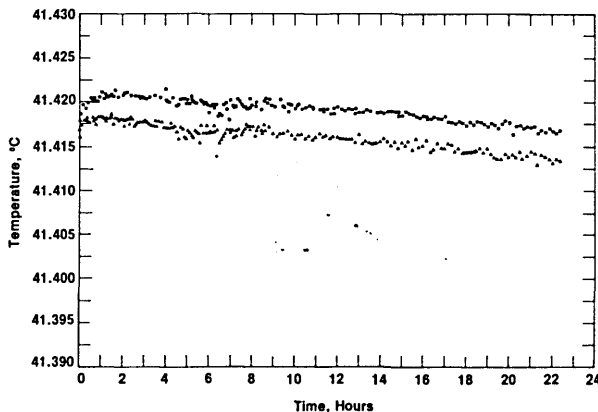

FIGURE 9. Temperature versus time profiles for the $KF \cdot 2H_2O$ transition recorded at 3.5 cm (■) and 2.5 cm (▲) below the surface of the mixture.
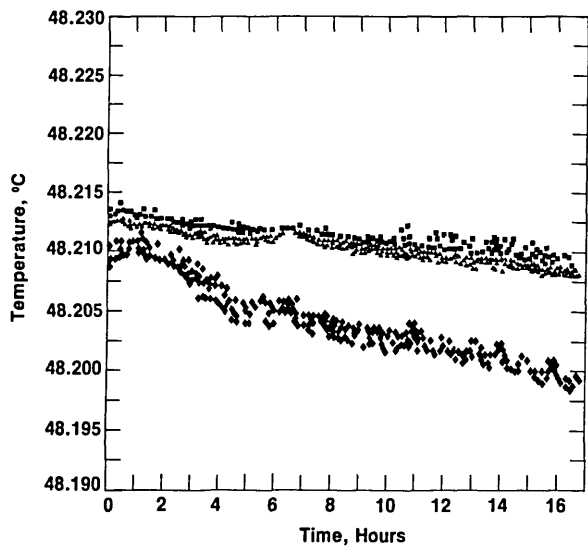
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FIGURE 10. Temperature versus time profiles for the $Na_2HPO_4 \cdot 7H_2O$ transition recorded at 3.5 cm (■), 2.5 cm (▲), and 1.5 cm (♦) below the surface of the mixture.
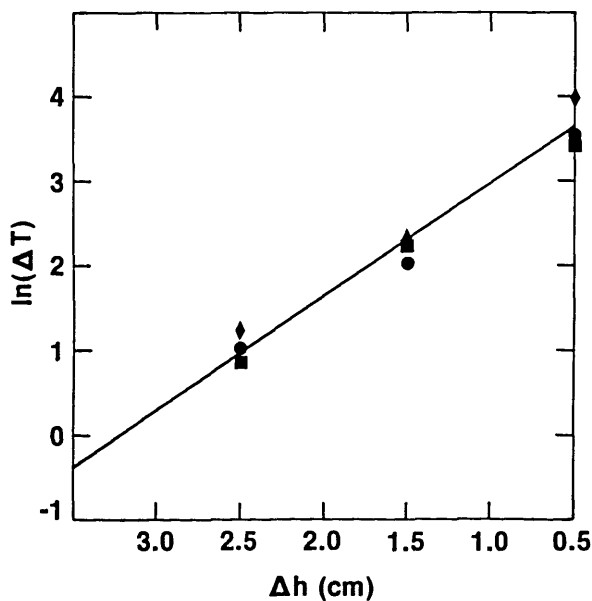

FIGURE 11. Temperature depression versus immersion depth at 0.9 cm (●), 1.8 cm (■), and 2.7 cm (♦) from the center of a 665 mL dewar containing a $Na_2HPO_4 \cdot 7H_2O$ transition.

the center of the 3.5 cm radius dewar. The results are shown in figure 11, where ΔT is the difference between the temperature of the thermistor at the indicated depth and that at a depth of 3.5 cm from the surface (0.5 cm above the stirrer). The roughly linear dependence of the data in figure 11

shows an exponential temperature change of the thermistor upon immersion in the thermistor well. These results indicate that the temperature at the depth at which the experimental measurements were made was depressed by heat loss to the surroundings by less than a millidegree Celsius.

3.4 Kinematic effects

The "true" transition temperature, whose stability is predicted by the Phase Rule, is maintained by the free energy available at the liquid-solid interface. Thus, in the non-equilibrium circumstance of constant heat loss from the vessel, there will be a temperature gradient from the interface through the liquid. Even if the mixture of solution and microcrystals is sufficiently well stirred to be homogeneous to a macroscopic thermometer, this average temperature is still somewhat lower than the interfacial temperature. The magnitude of the difference will depend upon the rate of heat loss, the thermal conductivity of the solution, the amount of surface available at the interface, as well as details in the mechanism of crystallization. Some of these effects were investigated in a series of experiments on the sodium sulfate: water system. This transition was studied at an ambient temperature of 24 °C in three vessels: a 665 mL dewar, a 265 mL dewar, and a 250 mL beaker insulated by styrofoam, as described previously. The data presented in figure 12 illustrate the results. The temperatures obtained in the large dewar, which should have the lowest heat loss, are the highest with the least fluctuations and longest period at maximum, while the converse is true for the temperatures measured in the relatively poorly insulated beaker.

To investigate the effect of interfacial area, we initiated sodium sulfate transitions with different quanities of decahydrate crystals of various sizes. It was difficult to control precisely the depth of supercooling for each of these experiments, so the results were not quantitative. Nevertheless, a few grams of granular decahydrate (crystals of 0.5 to 1 mm in diameter) resulted in a very extended recalescence and a rounded plateau, while a few grams of finely powdered material resulted in a rapid recalescence and a flat plateau.

An additional kinetic effect arises from the viscosity of the mixtures, due to heat generated as a result of mechanical stirring. The stirring is necessary to provide chemical and thermal homogeneity throughout the mixture. The plateau temperatures were not sensitive to stirring speeds between 200 and 600 rpm. At speeds less than 100 rpm, temperature gradients due to the settling of the more dense hydrate were observed and shorter plateau periods occurred, as shown in figure 13, whereas an increase in speed to greater than 600 rpm caused a step-like elevation in the measured temperature and a reversal in the direction of the transition.
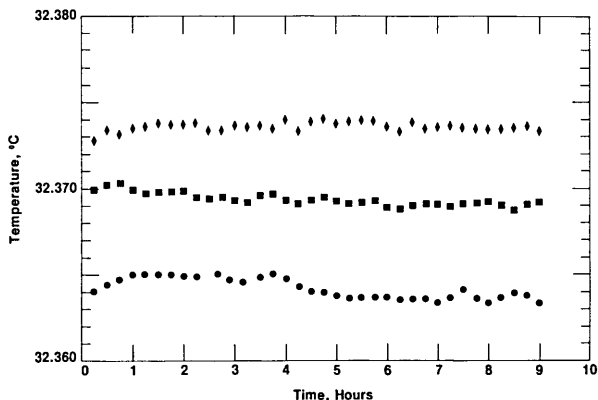
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FIGURE 12. Temperature versus time profiles for the Na₂SO₄·10H₂O transition in a styrofoam insulated beaker (●), a 265 mL dewar (■) and a 665 mL dewar (♦). Ambient temperature was 24 °C.
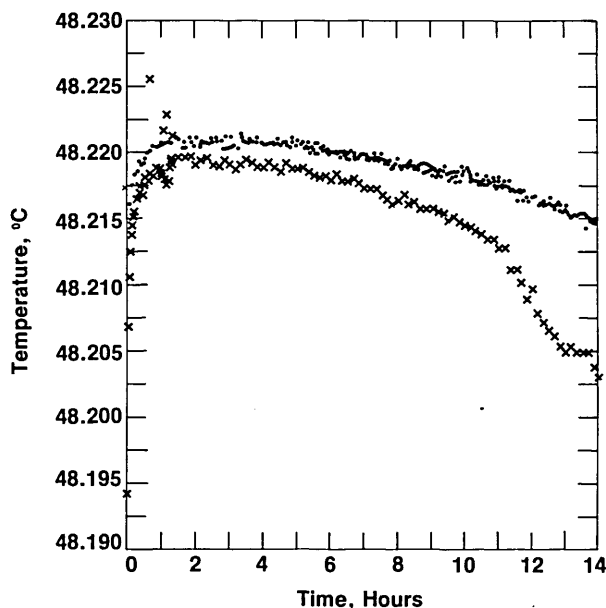
FIGURE 13. Temperature versus time profiles for the Na₂HPO₄·7H₂O transition at a slow, 100 rpm (×), and fast, 300 rpm (●), stirring speed.

4. Discussion of Results

4.1 Effects of atmospheric pressure

The experiments were conducted in air at atmospheric pressure, rather than at the quadruple point predicted by the Phase Rule. It is necessary, then, to assess the effects of pressure upon the transition temperature. This is given by the Clapeyron equation for a first order phase transition [43]:

$$\frac{dP}{dT} = \frac{L}{T\Delta V} \qquad (1)$$

where L is the latent heat of the transition, T is the transition temperature, and ΔV is the change in specific volume. We can apply this simple relation to each of the three salts with the following result:

Salt	dT/dP, °C/Pa
Na₂SO₄·10H₂O	$2 \cdot 10^{-8}$
KF·2H₂O	$23 \cdot 10^{-8}$
Na₂HPO₄·7H₂O	$8 \cdot 10^{-8}$

As a check on these calculations, consider first a more sophisticated calculation which takes into account the fact that two components, and hence four phases, are involved in the first order transition. This generalized Clapeyron equation takes the form [44]

$$\frac{dP}{dT} = \frac{\Delta S_1 - A\,\Delta S_u}{\Delta V_1 - A\,\Delta V_u} \qquad (2)$$

In this expression $\Delta S_{1,u} = S_{sol} - S_{1,u}$, where S_1, S_u are the specific entropies of the lower and upper hydrates, S_{sol} is the specific entropy of the solution, and $\Delta V_{1,u} = V_{sol} - V_{1,u}$ where V_1, V_u are the specific volumes of the lower and upper hydrates, and V_{sol} is the specific volume of the solution. The constant, A, is $A = (X_1 - X_{sol})/(X_u - X_{sol})$, where X_u, X_1, and X_{sol} are the weight fraction of upper hydrate, lower hydrate and the solution, respectively. These parameters are not available for all of the salts, but for sodium sulfate [45] the result is

$$\frac{dT}{dP} = 1.4 \cdot 10^{-8} \text{ °C/Pa} \qquad (3)$$

Tammann [46] has measured this quantity experimentally for sodium sulfate and obtained

$$\frac{dT}{dP} = 0.5 \cdot 10^{-8} \text{ °C/Pa} \qquad (4)$$

Note that the estimates formed using the Clapeyron equation, either eq (1) or its generalized version (2), are quite sensitive to the values of the specific volumes of the various phases.

Atmospheric pressure fluctuations over a period of 24 hours are typically less than ± 5 percent, so that differences in transition temperatures from sample to sample that might be attributable to such pressure changes are ± 0.10 m°C, ± 1.2 m°C, and ± 0.4 m°C for Na₂SO₄·10H₂O, KF·2H₂O, and Na₂HPO₄·7H₂O, respectively.

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4.2 Effects of impurities

The effects of impurities can be estimated by assuming that they are present in sufficiently low concentrations that the laws for ideal dilute solutions apply. Then the depression in the transition temperature, ΔT, is given by [43]

$$\Delta T = \frac{RT^2}{L}(U_1 - U_s) \qquad (5)$$

in terms of the gas constant, R, the heat of fusion, L, the transition temperature, T, and the impurity concentrations in the liquid, U_1, and in the hydrated solid phase, U_s. The "cryoscopic constant," $k = RT^2/L$, can be evaluated [45] for each salt hydrate as 9.9 for $Na_2SO_4 \cdot 10H_2O$, 32.9 for $KF \cdot 2H_2O$, and 18.5 for $Na_2HPO_4 \cdot 7H_2O$. The value of this constant for $Na_2SO_4 \cdot 10H_2O$ has been calculated using a more precise expression [47] and it has also been measured experimentally [48]. Both values were found to be in very close agreement with the one given above.

Applying eq (5) to the specific samples used in this study would require determining the impurities and their concentration, as well as knowing the relative solubility of each impurity in both the solid and the liquid phases. Since there is no simple way to obtain this information, we have taken the approach that an upper limit can be estimated by using the manufacturer's lot analysis and by assuming that all impurities are only liquid soluble. On this basis we have obtained the following estimates, using eq (5), for the depression in the transition temperatures due to impurities.

Salt Hydrate	Lot	Temperature Depression (m°C)
$Na_2SO_4 \cdot 10H_2O$	092	1.5
	558	2.0
	026	2.5
	824	>4.0
$KF \cdot 2H_2O$	165	4.0
	498	1.0
	533	4.5
	444	4.5
$Na_2HPO_4 \cdot 7H_2O$	150	2.1
	149	2.5
	478	3.4
	876	3.4

4.3 Stability and reproducibility of the transition temperature

From the results presented in table 5, it is apparent that the behavior of each system is quite distinctive, reflecting a different balance between heat generation by hydration and heat loss to the surroundings. The transition temperature of disodium hydrogen phosphate is about 48.2 °C, or some 24 °C above ambient, while that of potassium fluoride is about 17 °C above ambient, and for sodium sulfate, it is only about 8 °C above ambient. In addition, the latent heat of hydration of $Na_2HPO_4 \cdot 7H_2O$ is only 172 J/g, while for $KF \cdot 2H_2O$ it is 262 J/g and for $Na_2SO_4 \cdot 10H_2O$ it is 245 J/g [45]. It is, therefore, no surprise that the Na_2HPO_4 exhibits a much longer recalescence, as well as a shorter plateau, than either of the other salts. This effect may also be important in determining the observed variation in transition temperature since the variation within lots shown in table 5 is of the same order of magnitude as the lot to lot variations. These results suggest that there is a correlation between impurities and observed transition temperature for Na_2HPO_4, but the scatter of temperatures within a given lot is too great to establish this relationship precisely.

Potassium fluoride, on the other hand, shows much smaller variation of plateau temperature within a lot, though even this 0.002 °C variation could arise partly from variability in heat loss. Much more dramatic are the lot to lot variations, which in this case are as much as 0.04 °C. Although the listed impurities appear unable to account for these differences, it seems most likely that contamination is the cause. Potassium fluoride is a very reactive salt and it is difficult to control its level of purity.

Sodium sulfate is almost anomalously reproducible. On the basis of both pressure and impurity effects discussed above, variations of as much as 2 m°C appear possible. The variation actually observed was closer to 1 m°C.

5. Conclusions

The three salts studied exhibit transitions between different states of hydration for which the temperatures are stable to better than 2 m °C for several hours when the mixtures are well stirred in a dewar. The transition temperatures of all the salts are sufficiently reproducible for use as temperature fixed points, but since a few potassium fluoride temperatures were low by as much as 0.04 °C, the KF transition should not be used for high accuracy work. The disodium hydrogen phosphate transition temperatures, however, fell within a 0.007 °C range, while all the sodium sulfate transition temperatures were within a 0.002 °C range. The best values for the transition temperatures are: Na_2SO_4 to $Na_2SO_4 \cdot 10H_2O$—32.374 °C, KF to $KF \cdot 2H_2O$—41.422 °C, and $Na_2HPO_4 \cdot 2H_2O$ to $Na_2HPO_4 \cdot 7H_2O$—48.222 °C.

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