THE RARE EARTH METALS AND THEIR COMPOUNDS
Thermal Analysis of Rare Earth Nitrate Mixtures

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A method of analysis is proposed which utilizes the characteristic melting points of the hydrated salts and the liquidus curves of the binary salt mixtures for the estimation of the composition of rare earth mixtures. Several binary salt systems were investigated, employing very pure simple and double rare earth nitrates to provide basic information concerning the possibilities of the method.

It was pointed out by Jantsche (3) and by Friend (2) that the double magnesium nitrates and the simple nitrates of the cerium group rare earth elements exhibit relatively low congruent melting points. The double nitrates correspond in composition to the formula $Ce_2Mg_3(NO_3)_{12}{\cdot}24H_2O$, where the symbol Ce represents any one of the cerium group elements. Conclusive thermal analytical evidence for the existence of the double salts has been presented recently by Quill and Robey (4).

The simple nitrates crystallize in the form of the hexahydrate, $Ce_2(NO_3)_3{\cdot}6H_2O$ from water solution.

The quantitative analysis of most rare earth mixtures is a difficult matter, the most important methods in use today being the determination of the average equivalent weight, quantitative spectrographic analysis, and magnetic susceptibility measurements. All of these are very tedious, expensive, and yet not highly accurate.

Since the melting points are so characteristic for the various rare earth simple and double nitrates, it seems likely that the determination of the melting temperatures of rare earth nitrate mixtures might be a means to the quantitative estimation of the composition of the mixtures. This is possible because (1) a true solid solution results upon the mixing of corresponding rare earth salts and (2) knowledge of the behavior of solid solutions in general permits the conclusion that the melting temperatures of these mixtures are related in a simple fashion to their compositions.

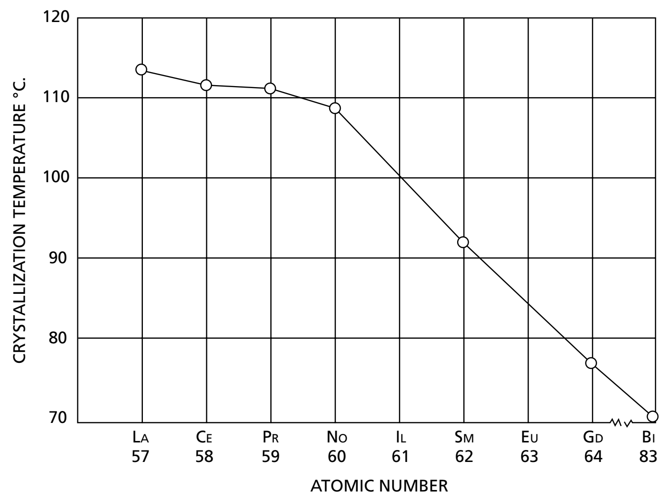

FIGURE 1 | Variation of Crystallization Temperatures (Melting Points) of Cerium Group Magnesium Double Nitrates with Atomic Number

The determination of the position of the liquidus curve of a binary rare earth salt system would yield the

TABLE 1 | Crystallization Temperatures of the Rare Earth and Bismuth Magnesium Double Nitrates

Atomic Number	Element	Temperature Jantach (3) °C.	Temperature This Investigation (4) °C.
57	La	113.5	113.5
58	Ce	111.5	112.0
59	Pr	111.2	.....
60	Nd	109.0	108.8
62	Sm	96.2	92.0
64	Gd	77.5	.....
83	Bi	.....	70.8

TABLE 2 | Crystallization Temperatures of Binary Systems

Bismuth and Samarium Magnesium Double Nitrates		Cerous and Samarium Magnesium Double Nitrates	
Samarium double salt *Weight per cent*	Temperature *°C.*	Samarium double salt *Weight per cent*	Temperature *°C.*
100.0	92.0	100.0	92.0
76.8	90.9	90.0	96.1
60.0	87.0	80.0	99.5
50.0	85.0	70.0	103.2
40.0	83.0	50.0	106.2
30.0	80.0	30.0	110.0
20.0	77.7	20.0	110.8
10.0	74.5	10.0	111.5
0.0	70.8	0.0	112.0

melting temperatures of all possible binary mixtures. Conversely, if the melting temperature of a mixture were determined, reference to the liquidus curve would yield the composition of the mixture. A thermal analytical method employing simple apparatus might be used in a very direct fashion to analyze rare earth mixtures and to follow the progress of separation of the rare earth elements in a fractional crystallization series.

In a method of analysis which is dependent upon an interpolation of a liquidus curve, the precision of the method will be a function of the difference between the crystallizing temperatures of the pure component salts. Accordingly, the melting points of the pure double magnesium nitrates of the cerium group elements as determined by Jantsch (3) and by the authors' investigations are given in Table 1. The values have been plotted in Figure 1 against the respective atomic numbers.

EXPERIMENTAL

Materials: The samarium and neodymium materials employed in this investigation were prepared from the pure oxides kindly lent by B Smith Hopkins of the Department of Chemistry, University of Illinois. The lanthanum nitrate was prepared as described in a previous paper (4). The arc emission spectra of these materials showed them to be free from foreign rare earth elements.

The cerium material was derived from the G.F. Smith Chemical Company's pure analytical ceric sulfate reagent. The cerium was purified by three successive precipitations by the well-known basic bromate method (a process described in all textbooks on the rare earth elements).

Ultimately the cerium was precipitated as the oxalate, the oxalate digested with concentrated nitric acid on the steam bath, the solution evaporated to a sirup and taken up in water containing a little hydrogen peroxide. The absorption and the arc emission spectra showed that no rare earth elements other than cerium composed the resulting material.

Baker's magnesium oxide of best purity with an unusually low calcium content was used in the preparation of the double magnesium salts. The magnesium and rare earth materials were dissolved in Grasselli's "chemically pure" nitric acid in the ratio of three to two gram-atomic weights, respectively, and the double nitrate was made to crystallize from the solution. A chemically pure grade of Baker's bismuth nitrate pentahydrate was employed for the preparation of the bismuth double salt.

The rare earth simple nitrates were crystallized from the nitric acid solution of the oxide, except cerium, in which case the oxalate dissolved. The resulting nitrate crystals were dissolved in water and recrystallized from water solution two or three times. All of the prepared salts were dried over 55 per cent sulfuric acid solution in a desiccator before use.

Procedure: Simple apparatus suffices for the thermal analysis of the low melting salts and their mixtures. The experimental method was that used by other investigators (1) with low melting salts. Briefly, it consisted of heating the prepared mixtures in Pyrex glass test tubes inserted in a well-stirred oil bath to a temperature somewhat above their melting temperatures. The constantly stirred mixtures were then permitted to cool, the rate of cooling being determined by means of a thermometer. The thermometer was comparatively calibrated with a Bureau of Standards certified instrument.

TABLE 3 | Crystallization Temperatures of Binary Systems

Point	Composition	Crystallization Predicted °C.	Temperature Observed °C.
A	30 per cent Sm salt Changed to	…	100.0
B	50.0 per cent Sm salt Changed to	104.2	104.0
C	20.0 per cent Sm salt	107.4	107.2

The temperature difference between the mixtures and bath was always kept as small as possible.

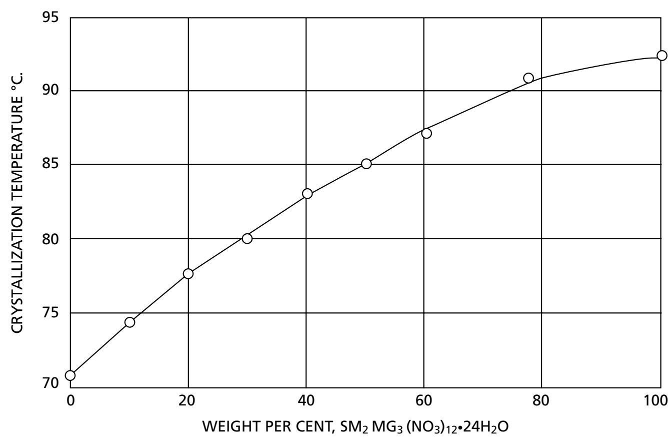

FIGURE 2 | Liquidus Curve of system Bismuth and Samaium Magnesium Double Nitrates.

BINARY SYSTEM

Samarium and Bismuth Magnesium Double Nitrates. Bismuth magnesium double nitrate is isomorphous in the crystalline state with the cerium group rare earth magnesium double nitrates. The double magnesium nitrates are salts which are employed largely in the separations of the cerium group elements by means of systematic fractional crystallization.

Urbain's modification of the usual methods of fractional crystallization consists in adding to the series a bismuth salt corresponding to the salt in crystallization. Since the salt possesses an intermediate solubility, it greatly aids the separation of the binary mixtures of samarium and europium which otherwise separate only slowly. Bismuth thus acts as a separating element. It is also a good separating element because it can be easily removed after use.

In adding bismuth magnesium nitrate to a series containing samarium magnesium double nitrate it is evident that certain fractions after repeated fractional crystallization will become binary solid solutions of the bismuth salt in samarium magnesium double nitrate. The results of the thermal analysis of a series of these binary mixtures of known composition are given in Table 2, which has been derived from time-differential temperature cooling curves of the various mixtures, and are plotted in Figure 2.

Slight losses of water were noted, especially among the higher melting mixtures on repeated determination. The crystallization temperature was identified by the "halt" point in the cooling curve produced by the formation of a crystalline precipitate, probably the anhydrous double salt. The mixtures remain fluid during this period. Final solidification does not occur until a much lower temperature is reached at which time only a negligible halt point is observed.

Samarium and Cerium Magnesium Double Nitrates. A study of the binary system cerium and samarium magnesium double nitrates would provide further information concerning the form of the liquidus curve. Naturally the data would be of little direct value since mixtures of serium and samarium are seldom encountered.

The results of the thermal analysis of the binary mixtures are given in Table 2 and plotted with the solid line curve in Figure 3.

A comparison of Figures 2 and 3 shows that the liquidus curves in both cases have practically the same form. It was found that both curves can be expressed approximately by the same mathematical equation. The composition of a mixture is related to the crystallizing temperature of the mixture by the equation

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$$P = 50\,[(f^2 - 4F)^{1/2} - f]$$

Where P is the weight percent composition of the mixture

$$f = \left[\frac{d^3 - 32d^2 - 63d - 16}{16}\right]$$

$$F = D^2 + \left[\frac{63 + 16d - d^2}{16}\right] D$$

d = the difference in degrees between the crystallizing temperatures of the two pure components, and
D = the difference in degrees between the crystallizing temperature of the mixture and that of the lower melting component

It is not unreasonable to assume that this empirical equation would be valid also for the liquidus curves of the other closely related rare earth double nitrate systems which possess a similar value of *d*; and that curves derived from this empirical equation might be used for the analysis of binary mixtures.

To test the validity of this method of analysis the composition of an "unknown" mixture was determined as follows:

1. The derived liquidus curve of the binary system neodymium and samarium magnesium double nitrates was plotted according to the above equation. It is given as the broken line curve in Figure 3.

2. A sample of crystals was removed from an intermediate portion of a fractionation series containing the mixed double magnesium nitrates of neodymium and samarium. The crystallization temperature of the sample was determined and found to be 100.0°. If the curve is the correct one, the composition of the mixture is represented by point *A* on the theoretical curve and the fraction is composed of approximately 30 per cent neodymium and 70 per cent samarium.

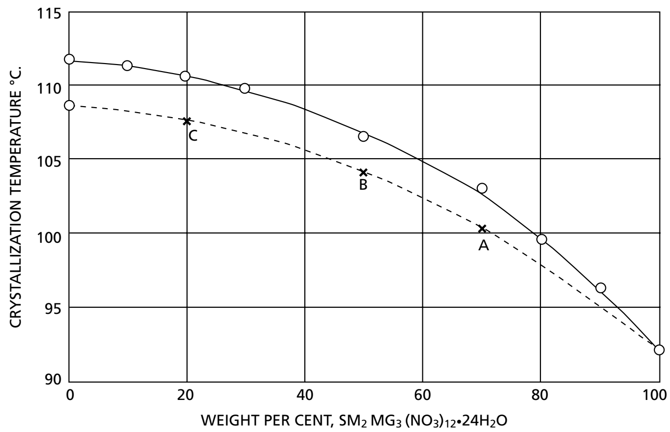

FIGURE 3 | Liquidus Curves. Solid line, cerous and samarium magnesium double nitrates. Broken line, neodymium and samarium magnesium double nitrates.

3. The composition of the sample was then changed successively by adding known weights of pure neodymium magnesium nitrate, the crystallization points redetermined and compared with the values predicted from the curve. The results are given in Table 3.

From this it is possible to conclude that the predicted curve falls very near to the true liquidus of the system.

Hexahydrated Cerous and Lanthanum Nitrates and Hexahydrated Cerous and Neoynium Nitrates. The simple nitrates also are amenable to study in binary systems with the view to employing the data for analyzing mixtures. The easily separable element, cerium, has been chosen as one constituent for the mixtures.

The melting points of the pure simple hexahydrated nitrates as determined recently by Friend (2) and by the authors are given in Table 4. These value have been plotted against the respective atomic numbers in Figure 4.

TABLE 4 | Solidification Temperatures of the Cerium Group Simple Hexahydrated Nitrates

Atomic Number	Element	Temperature Friend (2) °C.	Temperature This investigation °C.
57	La	65.4	66.5
58	Ce	…	51.4
59	Pr	56.0	…
60	Nd	67.5	64.1
62	Sm	…	79.5
64	Gd (98%)	…	87.0

TABLE 5 | Solidification Temperatures of Binary Systems

Hexahydrated Lanthanum and Cerous Nitrates		Hexahydrated Neodymium and Cerous Nitrates	
Hexahydrated lanthanum nitrate *Weight per cent*	Temperature *°C.*	Hexhydrated neodymium nitrate *Weight per cent*	Temperature *°C.*
100.0	66.5	100.0	64.1
90.0	63.5	90.0	62.8
80.0	63.0	80.0	62.0
70.0	61.9	70.0	60.0
60.0	60.0	60.0	58.0
50.0	58.4	50.0	56.0
40.0	57.5	40.0	53.8
30.0	56.4	30.0	53.5
20.0	55.0	20.0	53.0
10.0	53.7	10.0	51.8
0.0	51.4	0.0	51.4

The value of the solidification temperature of the gadolinium nitrate should be taken only as indicative of trend, since the perfectly white salt was labeled 98 per cent pure as purchased from the A.D. Mackay Company.

In observing the cooling curves of the molten hexahydrated nitrates, a slight halt is noted when a slight cloudiness makes its appearance. It is probably due to a lower hydrate. The major halt point, unlike the double magnesium nitrates, is found at the point of apparently complete solidification.

The solidification temperatures for the binary systems hexahydrated lanthanum and cerous nitrates and hexahydrated neodymium and cerous nitrates are given in Table 5. The liquidus curves have been plotted in Figure 5. Both liquidus curves are very roughly linear between the points representing the pure components. The irregular features of the curves are probably due to the effect of the formation of ceric cerium by autoxidation of the cerous nitrate at the elevated temperature. The colorless cerous salt and colorless mixtures containing the salt retained a slightly yellowish cast after heating. Titration of the ceric cerium thus formed by standard ferrous solution, using orthophenanthroline ferrous complex indicator in dilute sulfuric acid solution, showed that the ceric concentration never exceeded 1 per cent.

The necessity of obtaining the crystallized hexahydrated nitrates free from small amounts of residual impurities,

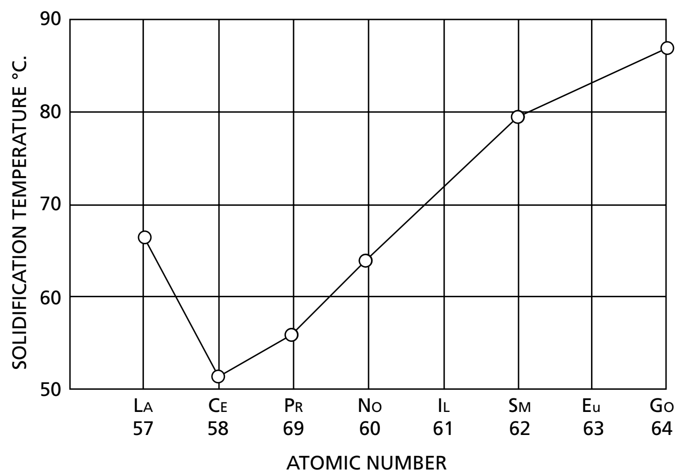

FIGURE 4 | Variation of Solidification Temperatures (Melting Points) of Hexahydrated Cerium Group Nitrates with Atomic Number

such as nitric acid, is emphasized by the data plotted in Figure 6. Less than 1 per cent of the acid lowers the solidification point several degrees.

An inspection of Figures 2 and 4 reveals that the following frequently associated pairs of simple nitrates and double magnesium nitrates possess crystallization temperatures sufficiently far apart to be useful in analysis through their binary liquidus curves: mixtures of the hexahydrated nitrates of (*a*) lanthanum and cerium, (*b*) lanthanum and praseodymium, (*c*) praseodymium and neodymium, (*d*) cerium and neodymium, and (*e*)

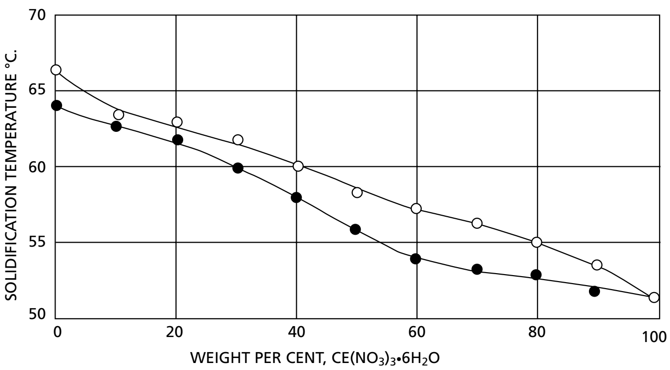

FIGURE 5 | Liquidus Curves

○ hexahydrated lanthanum and cerous nitrates
● hexahydrated neodymium and cerous nitrates

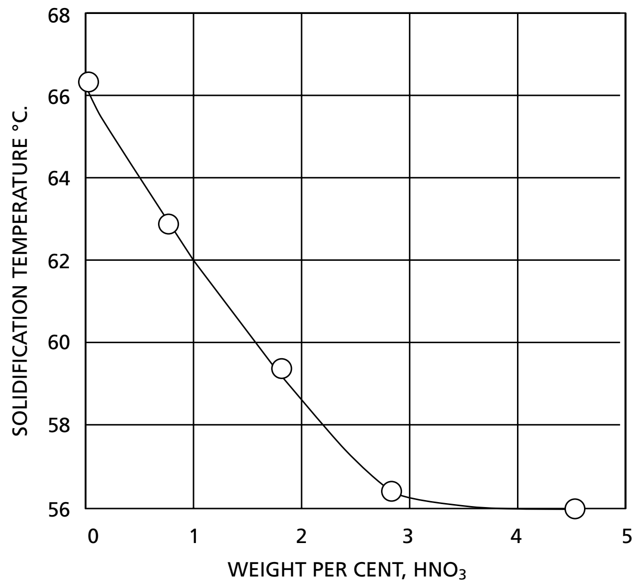

FIGURE 6 | Effect of Nitric Acid on Solidification Temperature of Hexahydrated Lanthanum Nitrate.

neodymium and samarium, and mixtures of the double magnesium nitrates of (*a*) samarium and neodymium, (*b*) samarium and bismuth, and (*c*) samarium and gadolinium.

SUMMARY AND CONCLUSIONS

The liquidus curves of certain binary systems of the simple and double magnesium nitrates of the cerium group of rare earth elements were investigated. All form a continuous series of solid solutions with corresponding rare earth and bismuth salts.

A method is proposed whereby quantitative estimation of the composition of rare earth nitrate mixtures can be accomplished by obtaining the freezing temperature of the nitrate mixture and the composition of the mixture determined by reference to the liquidus curve.

Further investigations of rare earth salts in binary, ternary, and even quaternary systems are obviously necessary in order to realize the full value of the method.

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Received June 4, 1937.