



Anion effects on magnesium flame emission
by Burton E Ginther

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree
of Master of Science in Chemistry

Montana State University

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Abstract:

A study of the comparative value of the various wave lengths for the measurement of magnesium emission intensity in flame photometry shows that the emission to background ratio is highest at 371 μ . The anion present has a great influence on the emission intensity at all wave lengths; the effects are more pronounced in the oxide band region (355 μ to 410 μ) than at the atomic line (285.2 μ). A study of depression curves recorded at various wave lengths shows that the detail of depression is similar at the principal wave lengths.

A new technique was developed for investigating the effects on emission intensity of adding varied increments of an additive to a standard solution in flame photometry. A device was designed which made possible an automatic and quantitative increase of an additive while holding the concentration of a standard constant and delivering a representative sample of this solution to the aspirator of the flame photometer burner. The emission intensity was continuously recorded, This technique simplifies and appreciably, reduces the time required for an investigation.

An extensive investigation of anion effects on magnesium emission showed that they are more complex than was formerly believed, possibly because of several contributing factors, A tentative explanation is presented for some of the observed anomalies. It is felt that additional information regarding high temperature chemistry is necessary for a more adequate explanation.

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ANION EFFECTS ON MAGNESIUM
FLAME EMISSION

by

BURTON E. GINTHER
/

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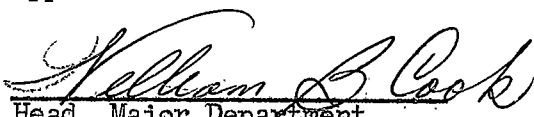
for the degree of

Master of Science in Chemistry

at

Montana State College

Approved:


Head, Major Department


Chairman, Examining Committee


Dean, Graduate Division

Bozeman, Montana
August, 1958

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I ABSTRACT

A study of the comparative value of the various wave lengths for the measurement of magnesium emission intensity in flame photometry shows that the emission to background ratio is highest at 371 mμ. The anion present has a great influence on the emission intensity at all wave lengths; the effects are more pronounced in the oxide band region (355 mμ to 410 mμ) than at the atomic line (285.2 mμ). A study of depression curves recorded at various wave lengths shows that the detail of depression is similar at the principal wave lengths.

A new technique was developed for investigating the effects on emission intensity of adding varied increments of an additive to a standard solution in flame photometry. A device was designed which made possible an automatic and quantitative increase of an additive while holding the concentration of a standard constant and delivering a representative sample of this solution to the aspirator of the flame photometer burner. The emission intensity was continuously recorded. This technique simplifies and appreciably reduces the time required for an investigation.

An extensive investigation of anion effects on magnesium emission showed that they are more complex than was formerly believed, possibly because of several contributing factors. A tentative explanation is presented for some of the observed anomalies. It is felt that additional information regarding high temperature chemistry is necessary for a more adequate explanation.

II INTRODUCTION

A survey of the literature shows that anion effects were long overlooked as interferences in flame photometry. This oversight has led to the development of analytical procedures of questionable accuracy for calcium and magnesium. These two elements give moderate emission when excited in the oxygen-hydrogen flame. Information now available indicates that the emission intensity will vary considerably with the anions present in aqueous solutions.

Three independently conducted investigations of anion effects on calcium emission intensity were recently reported (2, 7, 11). Anion effects were studied by adding increments of various anions, as acids, to a series of calcium chloride standards and noting the change in emission intensity when the resulting solutions were aspirated into the flame of a flame photometer. Since increments of hydrochloric acid produced no change in emission intensity, the hydrogen ion was considered to have no effect on emission intensity. Characteristic curves taken from data of Baker and Johnson (2), shown in figure 1, shows the effects of phosphate, sulfate, perchlorate, and chloride ions on the emission intensity of calcium. The marked depressing effect of phosphate was noted in all three investigations; this was apparently one of the dominant anion effects because the depressing effect persisted in the presence of other anions. As a means of avoiding errors due to phosphate interference in the flame photometric determination of calcium, it was suggested that phosphate ions be added to both standards and unknowns in sufficient quantity to depress the emission intensity to a minimum.

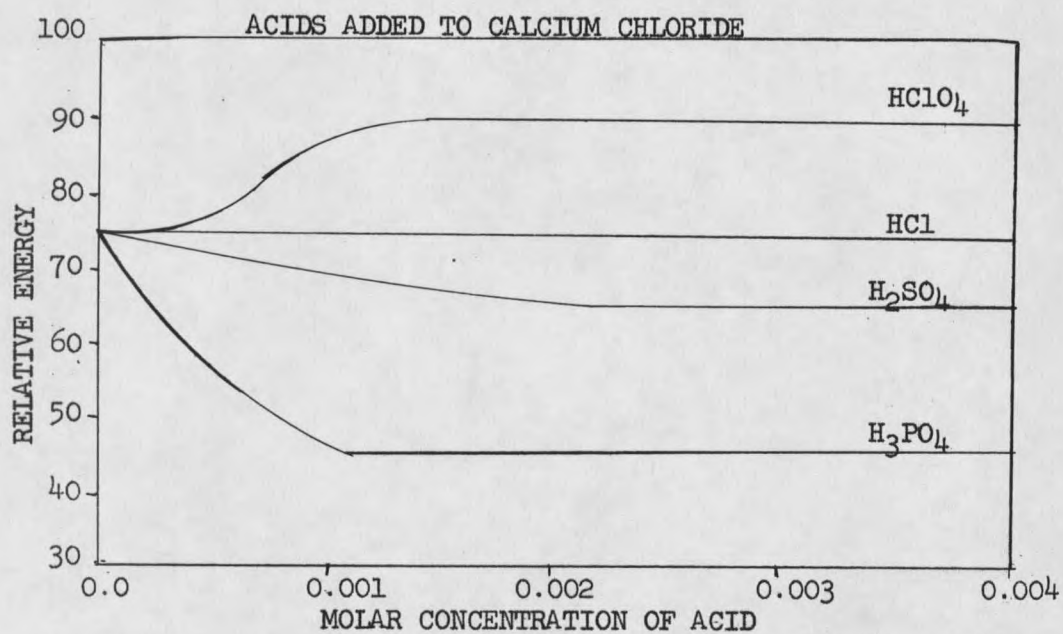
An investigation of anion effects on magnesium flame emission intensity was carried out by Anderson (1). The anion effects were studied by adding

increments of the corresponding acids to magnesium chloride standards prepared by reacting magnesium ribbon with hydrochloric acid. Figure 2, a partial reproduction of a graph presented by Anderson, shows the effects on emission intensity of the various concentrations of phosphoric, sulfuric, hydrochloric, and perchloric acids in 0.004 M magnesium chloride.

A comparison of figures 1 and 2 indicates that the anion effects on magnesium emission intensity are very similar to their effects on calcium emission intensity. In both instances it was observed that the presence of phosphoric acid caused a marked decrease, sulfuric acid caused a moderate decrease, hydrochloric acid caused little or no change, and perchloric acid caused a moderate increase in the emission intensity.

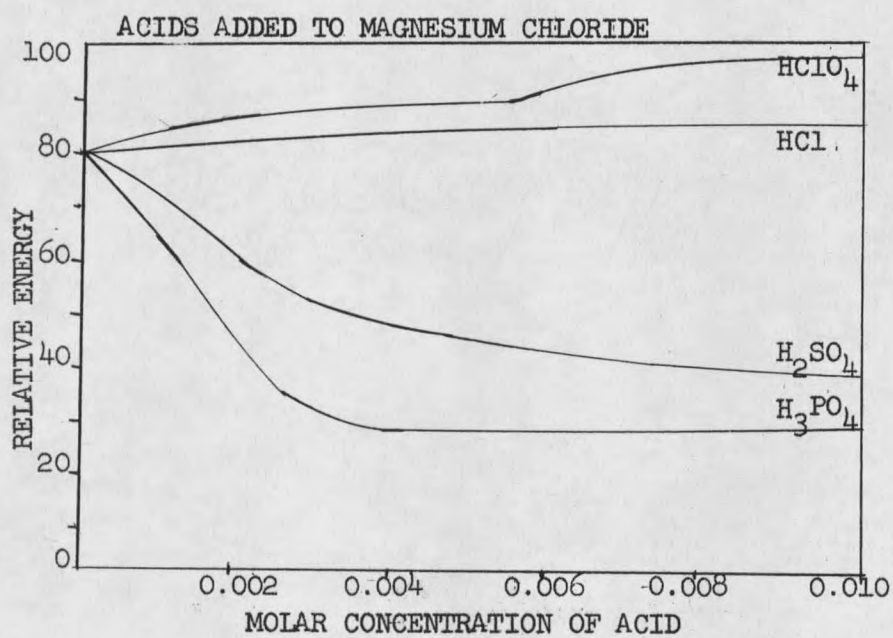
Magnesium emission intensity has been read at several wave lengths with little or no reason given for the selection. Some of the wave lengths that have been used are 285.2 mμ (5, 6, 8, 10), 371 mμ (1, 10) 383 mμ (9), and 385 mμ (6). One mention (8) was made of avoiding interference of iron by use of 285.2 mμ rather than 371 or 383 mμ.

The present investigation was undertaken to compare the usefulness of the various wave lengths in use, to determine if anion effects are the same at all useful wave lengths, and to study more critically the phosphate and sulfate ion effects on magnesium emission intensity measurements. A better understanding of these factors is of considerable importance in flame photometric determinations of magnesium.



data of Baker and Johnson (2)

Figure 1



data of Anderson (1)

Figure 2

III EXPERIMENTAL

A Beckman model DU spectrophotometer with a model 9200 flame attachment and a photomultiplier unit was the basic instrument used in the investigation. A number 4020 oxygen-hydrogen burner was used for excitation. Additional equipment used in the investigation was a spectral scan and recording attachment for the spectrophotometer. In conjunction with this a 1/3 second full-scale-travel, 0 to 10 millivolt Brown recorder was used. A tap key was placed in the recording circuit so the chart could be marked by shorting the circuit. In addition to this commercially available equipment an automatic mixing device and burner feed was designed and built for use in the investigation. Detailed description of this equipment will appear later in this section.

Standard solutions used in the investigation were prepared from analytical grade reagents and distilled water. Solutions, with the exception of magnesium stock solutions, were stored in pyrex glass stoppered volumetric flasks.

Four magnesium stock solutions were prepared as follows: Magnesium nitrate, chloride, acetate, and sulfate salts were weighed out into separate 500 ml volumetric flasks in sufficient quantities to make approximately one molar solutions of each. Magnesium concentration in these solutions was accurately determined by gravimetric procedure. The magnesium was precipitated as magnesium ammonium phosphate and after heating to 1000° C for several hours it was weighed as magnesium pyrophosphate. Determinations were run in triplicate on each solution with the maximum deviation from average being 0.021%. Pyrex glass storage containers were prepared by sealing

twelve inch extensions on the necks of 250 ml florence flasks. After the magnesium solutions were placed in the flasks, the tops were sealed with a glass blowing torch. To prepare standard solutions, the seal was broken, an aliquot was quantitatively removed by pipetting and the container was resealed. The working standards were made to 0.04 M concentration.

Approximately 0.05 M solutions of NaH_2PO_4 , K_2HPO_4 , $(\text{NH}_4)_2\text{HPO}_4$ and H_3PO_4 were prepared. After the phosphate concentration was determined colorimetrically, the concentrations of the solutions were adjusted to 0.05 molar.

Solutions of sulfuric, hydrochloric, nitric, acetic, and perchloric acids were prepared by diluting concentrated acids. These solutions were then standardized by titrating with a standard base and adjusting to the desired 0.05 M concentration.

Solutions of 0.05 M Na_2SO_4 , K_2SO_4 , NaCl , and KCl were prepared by dissolving the appropriate amounts of the salts in distilled water and diluting to the mark in volumetric flasks.

Spectral scans of the flame emission, obtained while aspirating 0.004 M solutions of each of the magnesium salts and distilled water, provided information about the relative values of the various wave lengths used in magnesium determinations. Figure 3 shows a set of scans where relative energy is plotted against wave length for the two ranges 280 mμ to 290 mμ and 350 mμ to 410 mμ. Relative energy is used in lieu of a better term. It is to be understood, however, that this is a measure of emission intensity. In preparing these scans the following procedure was used: (a) With the instrument properly warmed up, the photomultiplier sensitivity was set

to position 4, spectrophotometer check switch set to .1, wave length set to 371 mμ, the slit width set to .07 mm, and the scanner set to record. (b) The burner was lit. The oxygen tank pressure was set at 28 p.s.i. and the instrument pressure was set at 10 p.s.i. The hydrogen tank pressure was set at 10 p.s.i. and the instrument pressure was set at 5 p.s.i. (c) While aspirating a 0.004 M magnesium nitrate solution, the dark current and 100% adjust were set so a chart deflection of 5 units was obtained with the shutter closed and a moderate deflection was obtained with the shutter open. (d) The wave length was adjusted to 410 mμ, the scanner was turned on in the decreasing wave length position and the recorder chart was simultaneously turned on. (e) The scanner and the recorder chart drive were simultaneously turned off when the 350 mμ wave length was reached. (f) The wave length was adjusted to 290 mμ and the scanner and the chart drive were again turned on. (g) When the 280 mμ wave length was reached the scanner and the chart drive were turned off again. (h) The shutter was closed and the dark current was adjusted so the pen rode on the chart base line. The chart was manually turned back to the starting position. The dark current was then readjusted to give a chart deflection of 5 units. (i) A fresh solution was aspirated and scanned as before. Steps (h) and (i) were repeated for each of the 0.004 M magnesium solutions and for distilled water.

The magnesium spectral emission in the range 410 mμ to 355 mμ can probably be attributed to an oxide band with major band heads at approximately 382 -385 mμ and 371 mμ. The sharp peak at 285.2 mμ is attributed to an atomic line by Manna et al (8). Spectrographic data in the Hand Book of Chemistry and Physics (4) lists a magnesium line at 2852.13 Å and attributes

it to the neutral magnesium atom.

When one takes the relative energy reading of water (figure 3) as background and uses as emission only that relative energy above this level to calculate an emission-to-background ratio, it becomes apparent that the maximum value for this ratio will be obtained if the calculation is made at 371 mu. The difference in relative energy readings, at the various wave lengths for the several magnesium solutions, would appear to be due to the anion present since the solutions were of equal concentration. It also appeared, as shown in figure 3, that the anion effect was more pronounced in the oxide band than at the atomic-line wave length.

Since the anion effect appeared most pronounced and the emission-to-background ratio highest at the oxide band heads, the corresponding wave lengths seemed best for the investigation. The flame emission spectrum of each of the proposed additives was obtained over the region 350 mu to 410 mu. Only slight relative energy was detected when all solutions except those of sodium and potassium salts were aspirated into the flame. All sodium and potassium salt solutions gave substantial relative energy readings with the intensity increasing at the higher wave lengths. For reasons discussed previously and to minimize sodium and potassium interference, the 371 mu wave length was selected for the investigation.

The effect on emission intensity of increasing concentration of phosphoric and sulfuric acids in each of the magnesium standards was first studied by the conventional method. In this procedure, 5 ml of a 0.04 M magnesium standard solution was pipetted into each of a series of 50 ml volumetric flasks; progressively larger increments of a standard acid

solution were added to each successive flask. The solutions were then diluted to the mark with distilled water and mixed well. The concentration of magnesium in the solutions were 0.004 M and the concentration of acid varied from 0 to 0.016 molar. The relative energy was then measured with the flame photometer at a wave length setting of 371 mμ. The instrument was set to give a reading of 80 on the transmittance scale when a 0.004 M magnesium chloride solution was being aspirated and all other readings were taken at the same settings. Figure 5 shows the effect of increasing concentration of phosphoric acid in 0.004 M magnesium nitrate, chloride, acetate, and sulfate solutions. These curves are the result of repeated checks with very small concentration changes of the additive from one solution of a series to the next. The first data taken when phosphoric acid was added to magnesium chloride gave points significantly off of a curve with a single inflection point such as the one shown for a similar addition by Anderson (1). When smaller increments of phosphoric acid were used, the area of double inflection was discovered. It would appear that Anderson missed part of the detail in his investigation by observing an insufficient number of points. The curves presented in figure 5, in each instance, were prepared from readings taken on two series of solutions made from separately prepared magnesium standard solutions. The accuracy of the magnesium chloride and acetate curves was further proved by readings taken on a third series prepared with lithium chloride added as an internal standard. Readings were taken on this series using the internal standard technique to obviate such possible variables as flame fluctuation, viscosity changes, and instrumental sensitivity changes. All series of data obtained for each system gave the same detail and corresponding readings agreed to

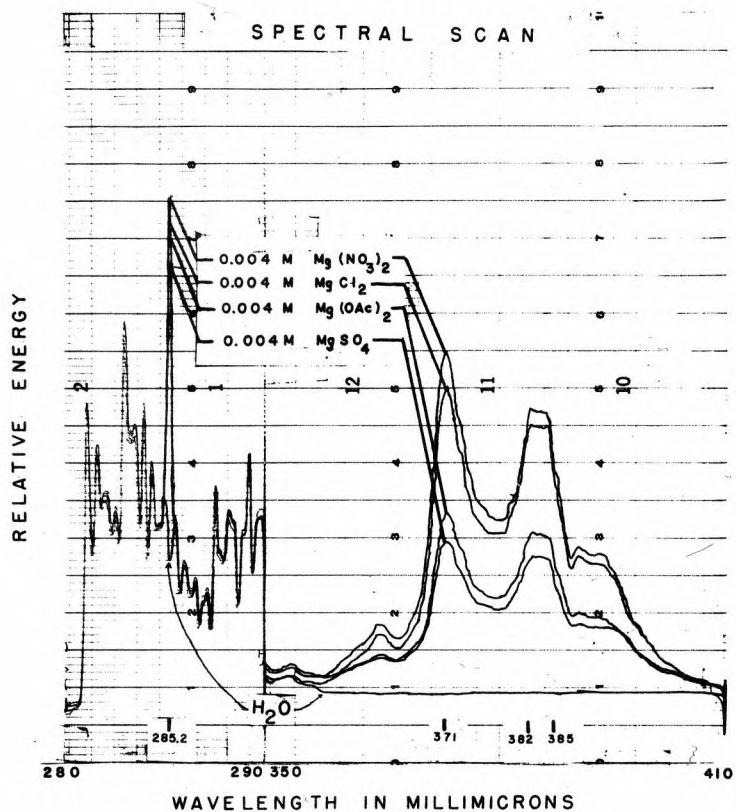


FIGURE 3

BURNER FEED ASSEMBLY

- A ADDITIVE RESERVOIR
- B NEEDLE VALVE & FLOAT
- C MIXING CHAMBER
- D MAGNETIC STIRRER
- E FEED TUBE
- F BURNER
- G OVERFLOW DRAIN

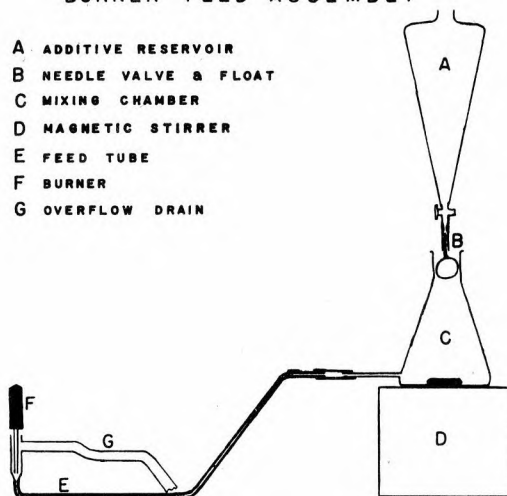


FIGURE 4

within 1 percent of average. Figure 6 shows the observed effects of increments of sulfuric acid in the 0.004 M magnesium standards. The procedure used in taking data for these curves was the same as that used in taking data for curves in figure 5 except that the internal standard technique was not used for any of the readings.

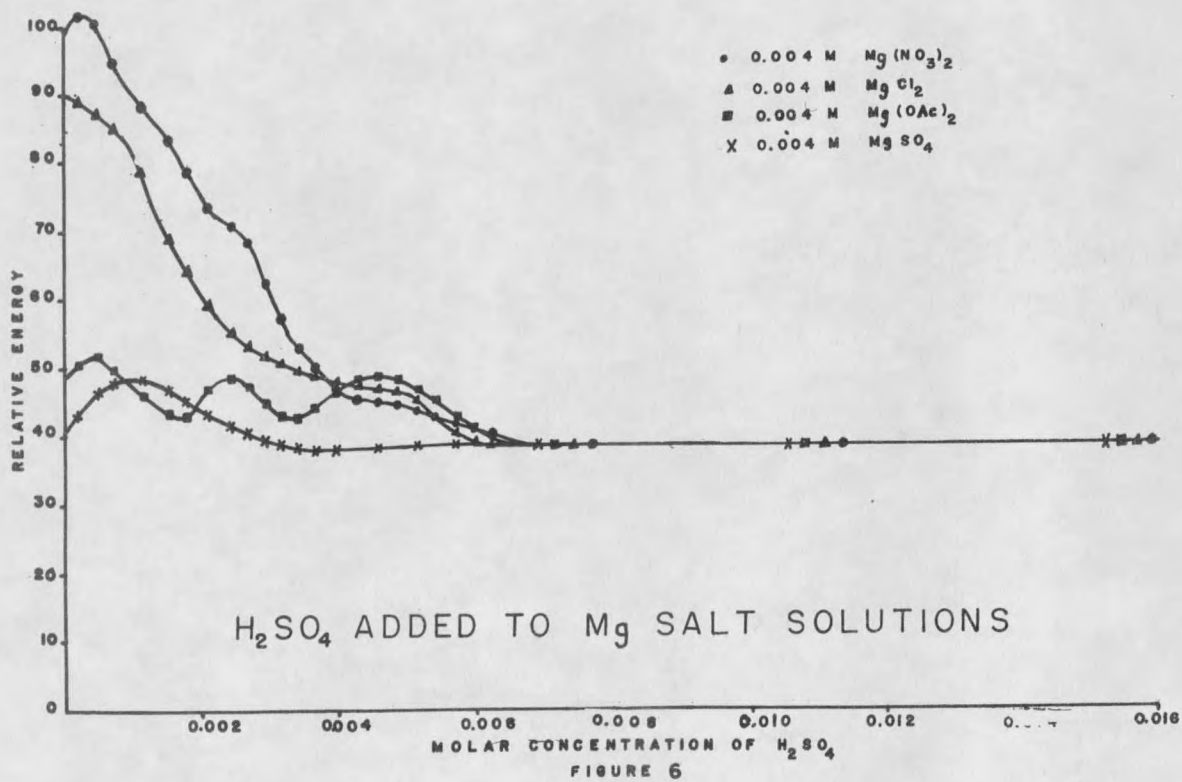
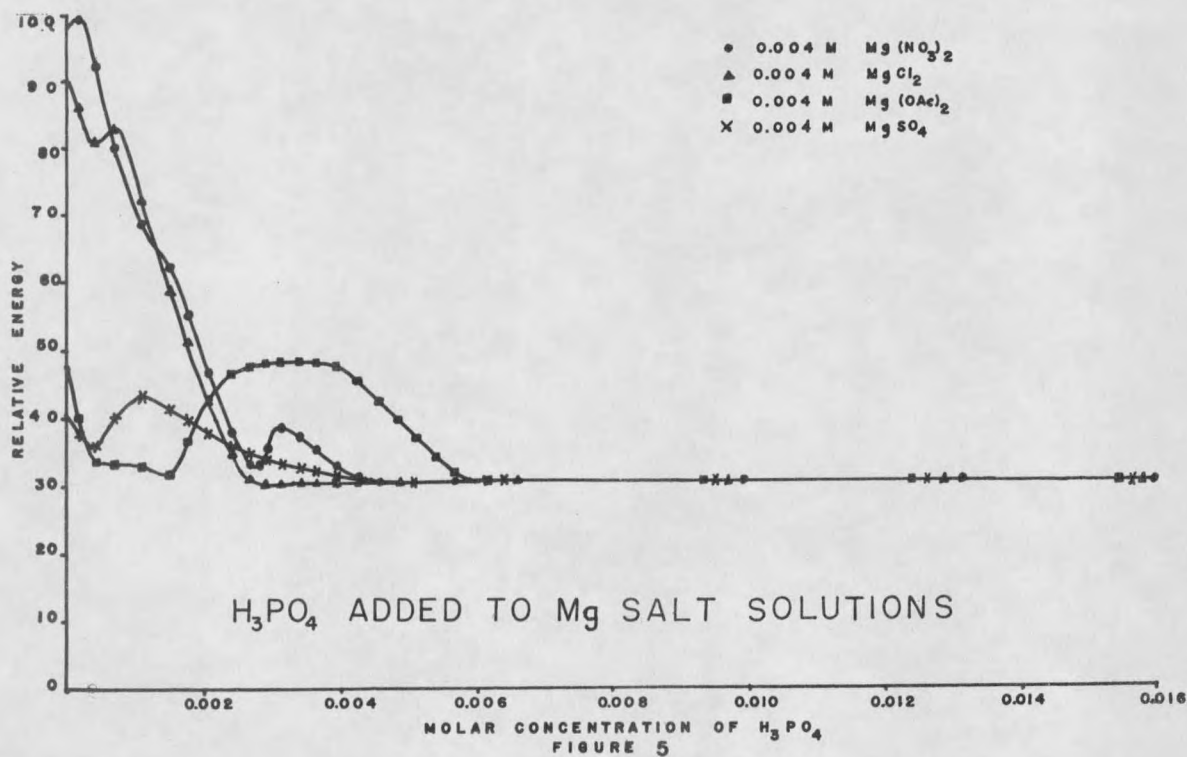
The extreme irregularity in the various curves was interpreted to mean that several factors rather than a single one were affecting the emission intensity of magnesium.

It became apparent, at this point, that a more rapid technique for making extensive additional examinations was virtually mandatory. The time requirements to critically carry out an extensive investigation by conventional procedure would have been prohibitive. By making the proper adaptations it was felt that the technique of Bock and Nan-Sing Ling (3) of automatically changing the composition of an eluent liquid in elution chromatography could be applied in developing a rapid technique for investigations in flame photometry. The requirements of the proposed technique were these: (a) a method of holding the concentration of one component of a solution constant while varying the concentration of another component in such a way that its concentration could be determined at any time, (b) a method of continuously delivering a representative sample of this solution to the aspirator of the burner on the flame photometer, and (c) a method of continuously recording the relative emission intensity. The spectral energy recording attachment provided a means of continuously recording the emission intensity. The other two requirements were satisfied by the burner feed assembly shown in figure 4.

The burner feed assembly, which consists of (A) an additive reservoir, (B) a needle valve and float assembly, (C) a mixing chamber, (E) a burner-feed-tube, and (G) an overflow drain, was specially designed and built for the purpose. The additive reservoir was a 250 ml separatory funnel. The needle valve and float assembly was made by constricting a short section of 6 mm glass tubing and then grinding the tip of a slightly drawn 3 mm glass rod into this constriction to make a ground glass joint. The other end of the rod was sealed to a thin walled glass bubble blown to fit loosely into the neck of the mixing chamber. The mixing chamber was made by sealing a short length of 6 mm glass tubing as a side-arm near the bottom of a 250 ml erlenmeyer flask. Mixing was provided by a magnetic stirrer. The burner-feed-tube and overflow unit was made by sealing a length of capillary tubing to a short length of 10 mm tubing and then sealing a length of 10 mm tubing near the open end of this as an overflow drain. The tubing was then bent so that it could be slipped over the aspirator tube of the burner with both the capillary feed-tube and the overflow tube extending through the sample-introduction-opening of the burner housing door. The outer end of the capillary tube was connected to the mixing chamber side-arm with a short length of rubber tubing. A pinch clamp provided a convenient means of regulating the flow of solution through the apparatus.

Operational procedure for the automatic technique was as follows:

- (a) The mixing chamber was filled with a standard solution which was allowed to fill and flush the burner feed assembly.
- (b) The additive reservoir was filled with 250 ml of a solution equal in standard concen-



tration to the solution in the mixing chamber and 0.01 M with respect to the desired additive. (c) With the spectrophotometer warmed up, the slit width was set at .07 mm, the wave length was set at 371 mμ, the photomultiplier sensitivity was set to position 4, the spectral energy recording attachment was set to record, and the recorder chart speed was set at 2 inches per minute. (d) The burner was lit and gas pressures were adjusted. (e) the pinch clamp was removed to allow standard solution to flow through the burner feed assembly. The dark current and 100% adjust were set to give a chart deflection of 5 units with the shutter closed and a suitable deflection with the shutter open. (f) The pinch clamp was replaced, the mixing chamber was refilled with standard solution, and the stopcock on the additive reservoir was opened. (g) The magnetic stirrer was started and set at position 3. (h) The pinch clamp was removed, and the time that the first additive entered the mixing chamber was recorded by tapping the shorting key. (i) The entrance of the last of the additive into the mixing chamber was recorded by again tapping the shorting key. (j) The instrument was shut down 15 seconds after the last of the additive entered the mixing chamber. The graph on the recorder chart gave a plot of relative energy versus time. The time factor was converted to concentration of additive by either a mathematical calculation or by a comparative method.

The mathematical calculation was made relatively easy by assuming: (A) the flow rate remains constant during addition, (B) complete and uniform mixing is obtained in the mixing chamber, and (C) a representative sample of the solution is delivered unchanged from the chamber to

the aspirator. Experimental data showed that these assumptions are valid.

The mathematical calculation of concentration of additive at any time was made by use of equation 7 arrived at as follows:

$$\frac{dx}{dt} = R C_1 - R C_2 \quad \underline{1}$$

x = number of moles of additive in the mixing chamber

t = time in minutes

R = the flow rate, experimentally found to be 0.0368 l. per minute

C_1 = the concentration of the solution entering the chamber (0.01 M)

C_2 = the concentration of the solution leaving the chamber ($\frac{x}{.25}$)

By substitution and rearrangement equation 1 becomes,

$$\frac{dx}{dt} = .0368 \left(.01 - \frac{x}{.25} \right) \quad \underline{2}$$

or

$$\frac{dx}{dt} = .147 \left(.0025 - x \right) \quad \underline{3}$$

separating variables

$$\frac{dx}{.0025 - x} = .147 dt \quad \underline{4}$$

and integrating

$$- \ln (.0025 - x) = .147 t - C \quad \underline{5}$$

When $t = 0$, $x = 0$ so $C = - \ln .0025$

6

By substitution and rearrangement

$$x = .0025 (1 - e^{-.147 t}) \quad \underline{7}$$

The molar concentration can then be obtained by dividing the value found for x by 0.25, the volume of the mixing chamber.

The validity of equation 7 was checked as follows: With the mixing chamber full of distilled water and the reservoir full of 0.01 M $MgCl_2$, the procedure given on page 17 was followed. Data of this experiment

is shown in figure 8. Points on this curve were compared to points of equal energy on the standard curve in figure 7. The data of figure 7 was obtained at the same instrument settings as were used in obtaining the data shown in figure 8. Theoretical values, as calculated with equation 7 above, and the observed values agreed to within one per cent. The precision of the automatic technique was therefore considered comparable to the manual technique. The automatic technique had the following advantages: (a) continuous recording, (b) a need for only two solutions, and (c) a much more rapid method of taking data.

The automatic technique was then used for investigating the effects of anions on magnesium emission intensity. All magnesium solutions were 0.004 M, and 250 ml. of a 0.01 M additive solution was used. The instrument was set to give the following chart deflections: 5 units for dark current and 85 units for the 0.004 M magnesium solution, unless otherwise stated.

Figures 9 - 12 show the effects on emission intensity of increasing concentration of phosphoric acid in each of the magnesium standards. It will be noted that the results are essentially the same as those presented in figure 5. The graphs have increasing concentration plotted from right to left making comparison slightly difficult. The concentration range of additive covered in the instrumental plots was reduced from that covered in the manual plots so that rapid changes in emission intensity, due to slight changes in concentration of additive, could be detected better. Instrument sensitivity was changed for each magnesium standard so that the greatest change in relative energy could be observed.

Phosphate was next added to each of the magnesium standards as three different salt solutions in an attempt to determine if hydrogen ion concentration was responsible for some of the observed inflections. Figures 13 - 16 show the effects on emission intensity of increasing concentration of NaH_2PO_4 in the magnesium standards. The effects on emission intensity of increasing concentration of K_2HPO_4 in the magnesium standards is shown in figures 17 - 20. The marked increase in relative energy readings at the higher concentrations of sodium and potassium salts is believed to be due to emission by these two elements.

The effects on emission intensity of increasing concentration of $(\text{NH}_4)\text{H}_2\text{PO}_4$ in the magnesium standards are shown in figures 21 - 24. It will be noted that these graphs are identical to those shown for increasing concentrations of phosphoric acid indicating that the ammonium ion either has no effect or the same effect as the hydrogen ion.

As noted above, upon the addition of a salt the emission intensity may be affected by both cations and anions. So-called "net effect curves" were therefore prepared in an attempt to eliminate the effect of the added cation and to facilitate comparison of anion effects. In phosphate systems the phosphoric acid curves were used as the standard of comparison. In sulfate systems sulfuric acid curves were used as the standard of comparison.

The means of obtaining "Net Effect Curves" will be illustrated by example (refer to figure 25).

- (1) The lower curve labeled H_3PO_4 shows the emission intensity recorded as phosphoric acid concentration was increased in distilled water.

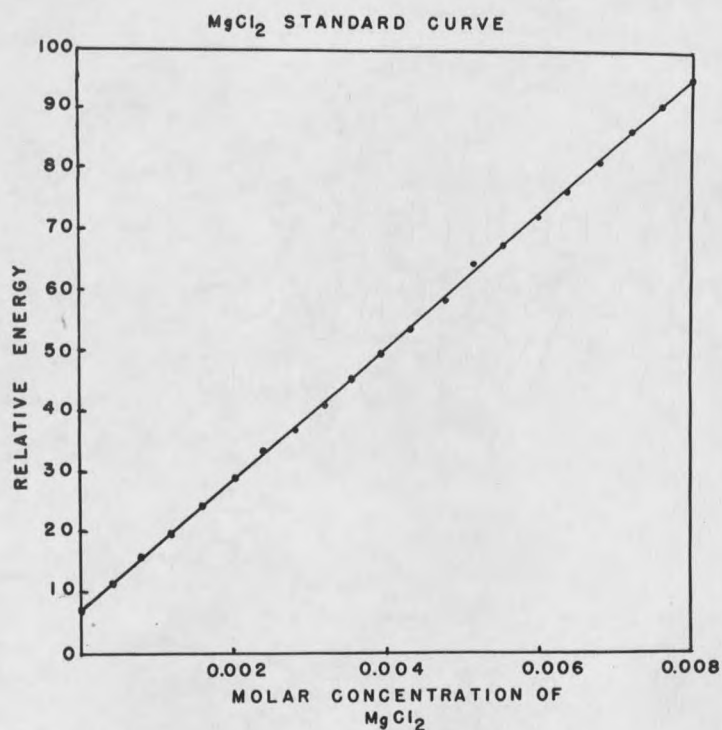


FIGURE 7

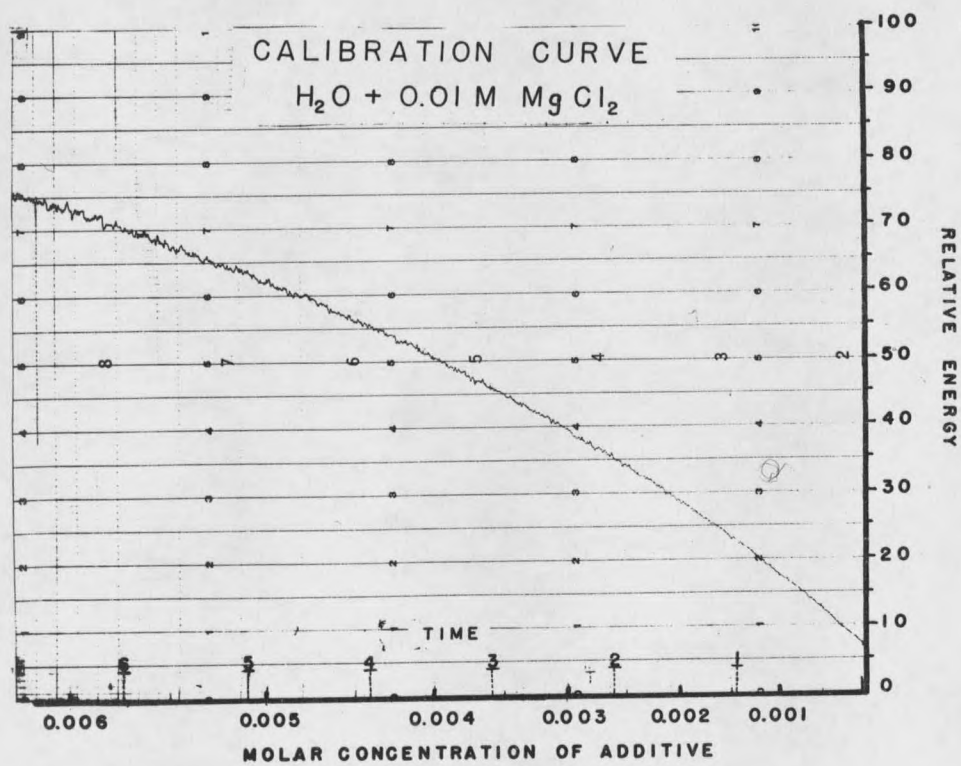


FIGURE 8

- (2) The lower curve labeled NaH_2PO_4 shows the emission intensity recorded as NaH_2PO_4 concentration was increased in distilled water.
- (3) The upper curve labeled H_3PO_4 shows the emission intensity recorded as phosphoric acid concentration was increased in $0.004 \text{ M Mg}(\text{NO}_3)_2$.
- (4) The upper curve labeled NaH_2PO_4 shows the emission intensity recorded as NaH_2PO_4 concentration was increased in $0.004 \text{ M Mg}(\text{NO}_3)_2$.
- (5) The curve labeled Net was obtained by subtracting from (4) the values of the difference of (1) and (2).

"Net Effect Curves" for increasing concentration of NaH_2PO_4 , figures 25 - 28, and K_2HPO_4 , figures 29 - 32 in the magnesium standards are shown.

Net sulfate effect curves were prepared in a similar way. "Net Effect Curves" for increasing concentration of Na_2SO_4 , figures 33 - 36, and K_2SO_4 , figures 37 - 40, in the magnesium standards are shown. Since the addition of sulfates to MgSO_4 was found to produce a marked increase in emission intensity it was necessary to lower the starting point to a chart deflection of 70 units. This was done by adjusting the dark current, thus not affecting the sensitivity significantly.

A brief study of the effects of perchloric acid on magnesium emission intensity was made because of its extensive use in wet ashing biological samples. Figures 41 - 44 show the effects of increasing concentration of perchloric acid in the magnesium standards. Because of expected enhancement of emission intensity by the perchloric acid, magnesium acetate and sulfate were both run at the same instrument settings as were used for magnesium nitrate.

The effects on emission intensity of increasing concentration of

nitric acid in magnesium nitrate, figure 45; hydrochloric acid in magnesium chloride, figure 46; acetic acid in magnesium acetate, figure 47; and sulfuric acid in magnesium sulfate, figure 48, are shown.

To show that anion effects are similar at all wave lengths two representative graphs recorded at 285.2 μ are shown. The effects on emission intensity of increasing concentrations of phosphoric acid in magnesium nitrate and acetate are shown in figures 49 and 50. It will be noted that the same detail is shown in these as in similar systems recorded at 371 μ even though the effects are less marked.

IV DISCUSSION

A comparison of data presented by Anderson (1) and data of the present investigation shows generally good agreement. A marked difference in detail is observed when the graphs showing the results of adding phosphoric and sulfuric acids to magnesium chloride are compared, but their magnesium to anion ratio and their per cent depressions are nearly identical. Comparison of the data of the two investigations for the addition of perchloric acid to magnesium chloride appears to show identical results over the region of common investigation. A major point of disagreement is noted when the data for the addition of hydrochloric acid to magnesium chloride from the two investigations are compared. Where Anderson's data show a slight increase in magnesium emission intensity as the hydrochloric acid concentration increases, data taken during the present investigation show a rapid moderate increase in emission intensity followed by a constant emission level as the acid concentration increases.

A close examination of Anderson's work indicates that the curves presented were drawn with eleven evenly spaced plotted points as guides. It was further noted that the curves do not pass through all of the plotted points. Close observation shows that the points which do not fall on the curves are in positions shown to exist in the present investigation. In the present investigation some areas of inflection required ten times the points taken by Anderson to clearly define the detail when studied by the conventional technique. This would appear to explain part of the differences in detail.

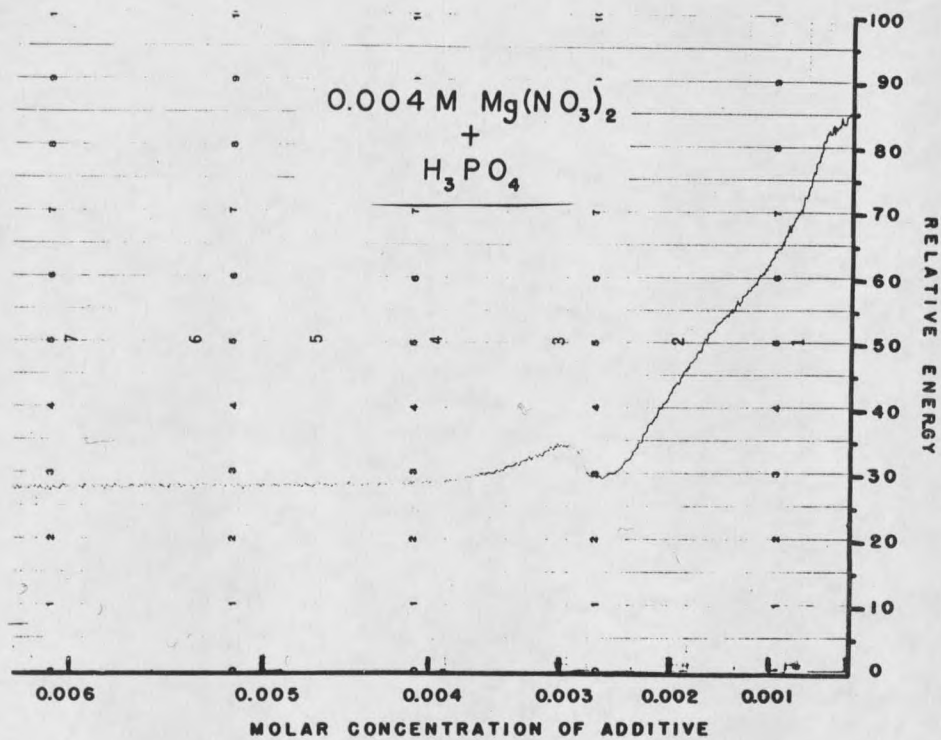


FIGURE 9

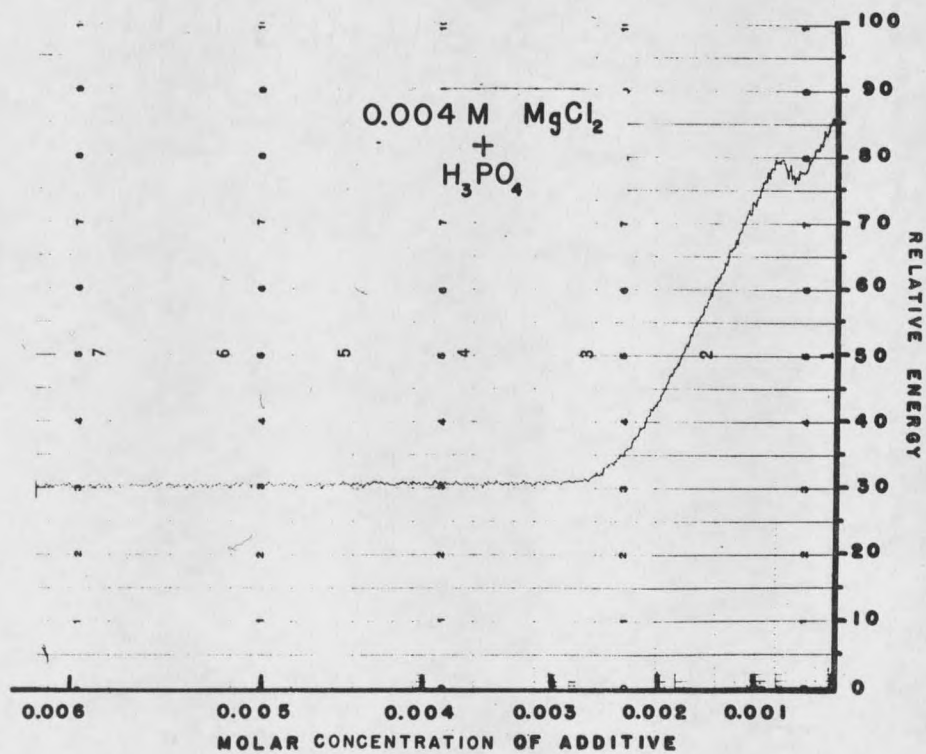


FIGURE 10

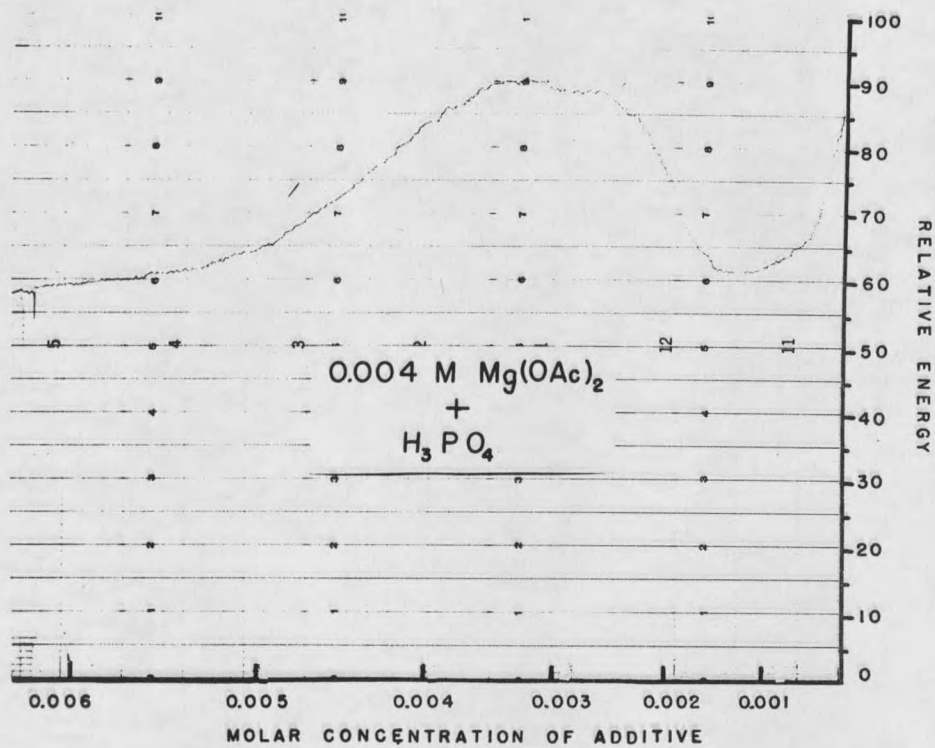


FIGURE 11

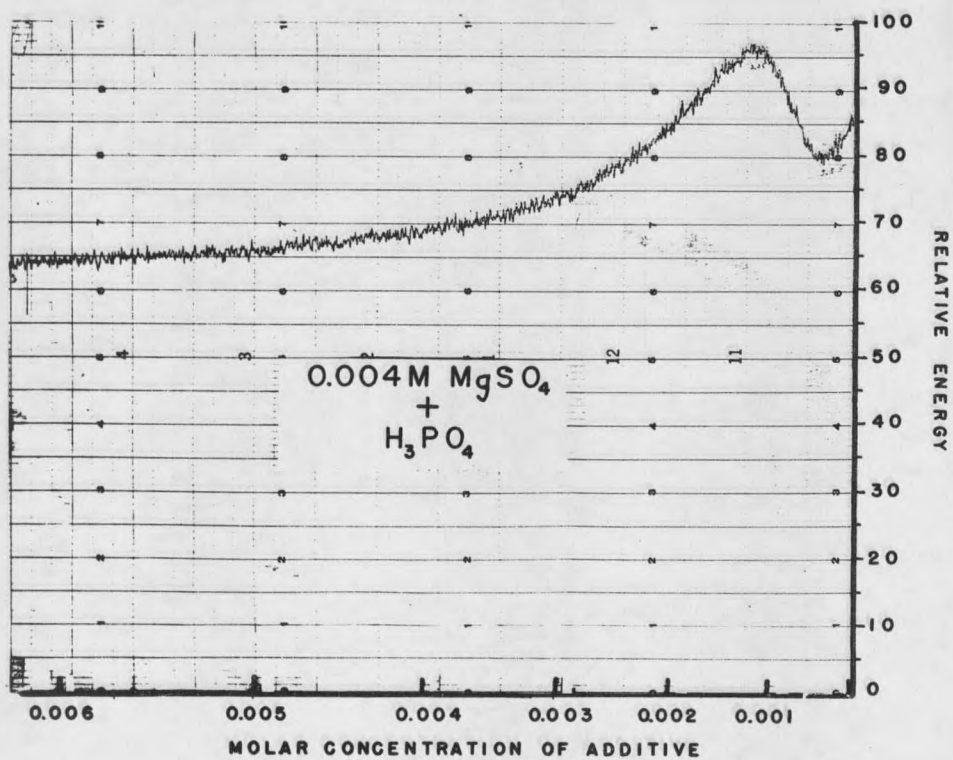


FIGURE 12

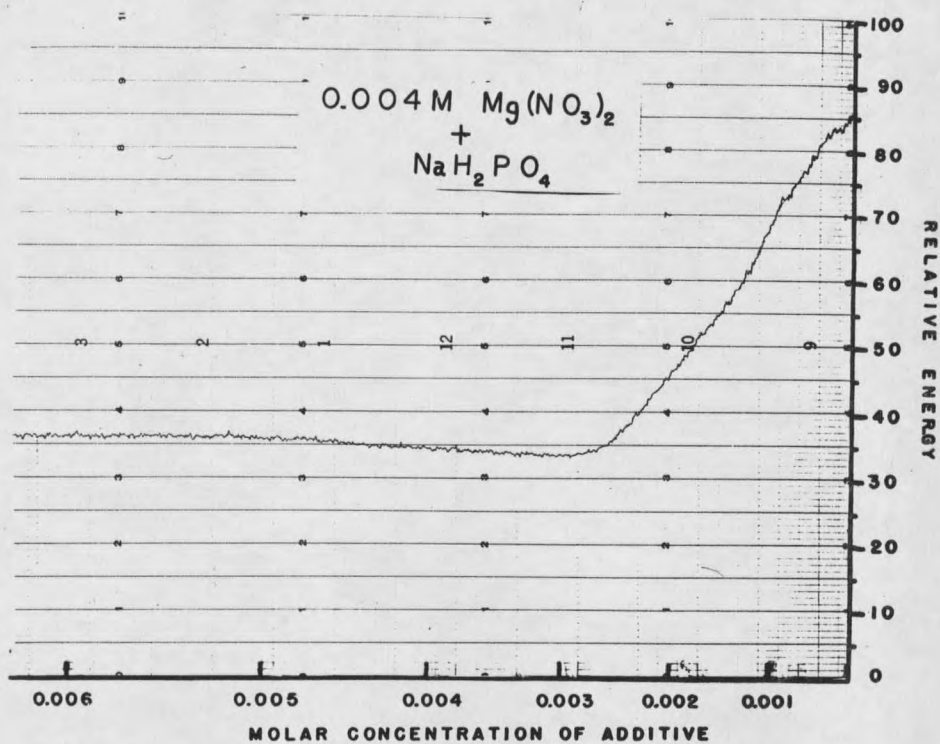


FIGURE 13

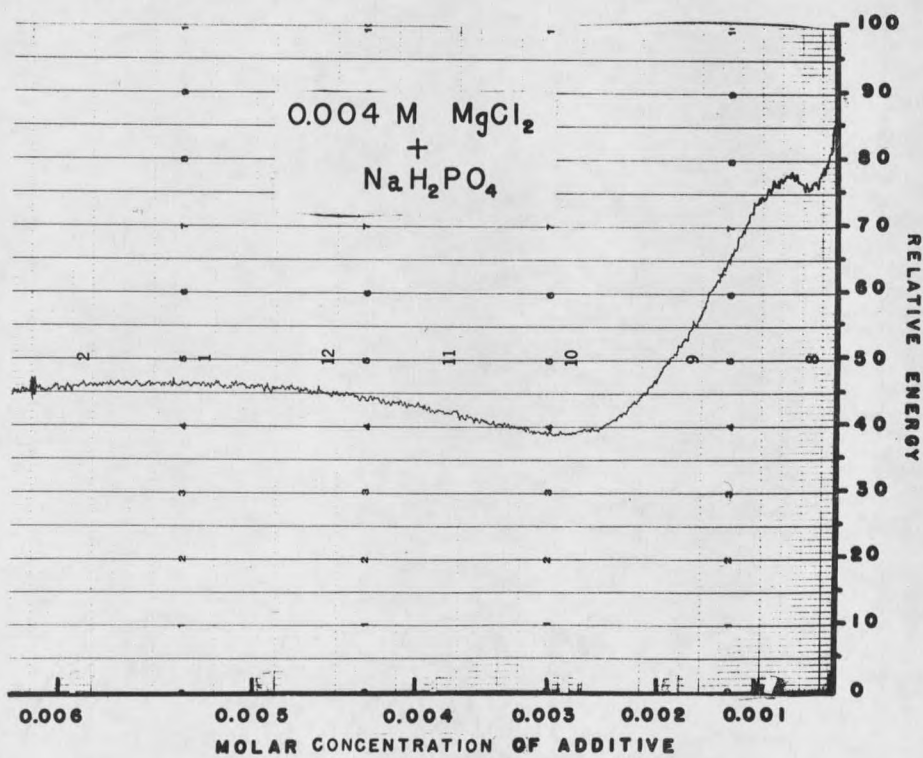


FIGURE 14

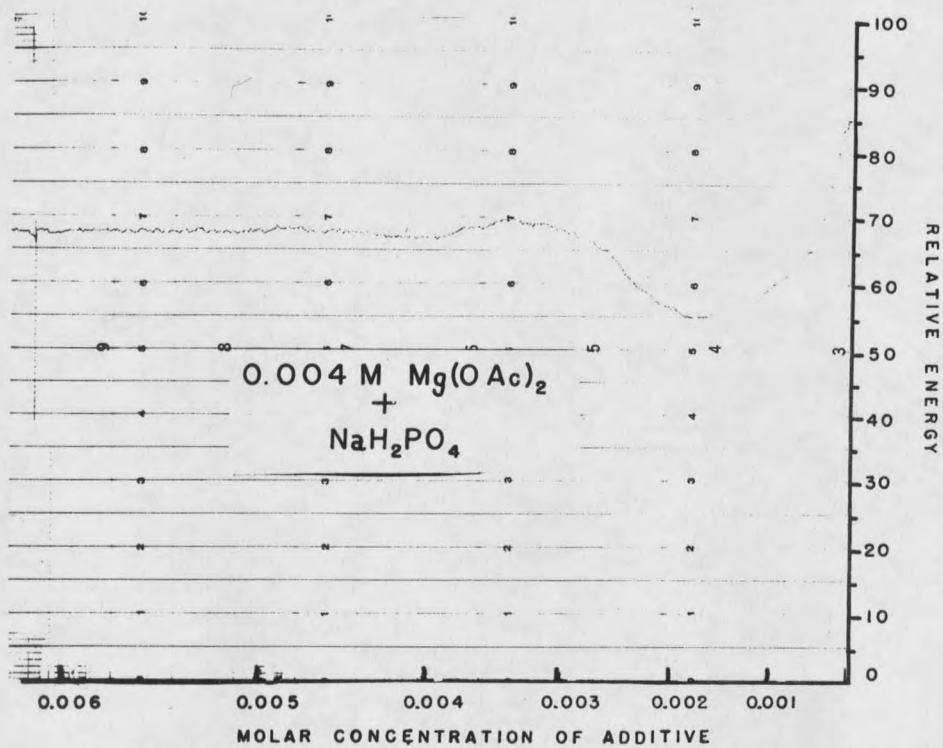


FIGURE 15

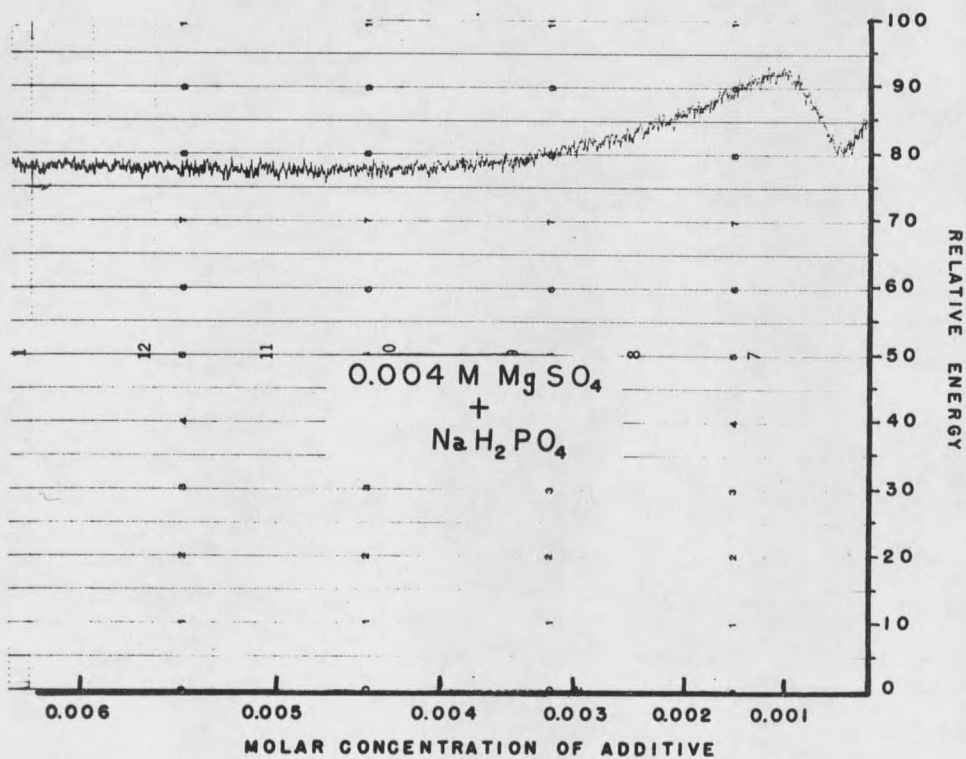


FIGURE 16

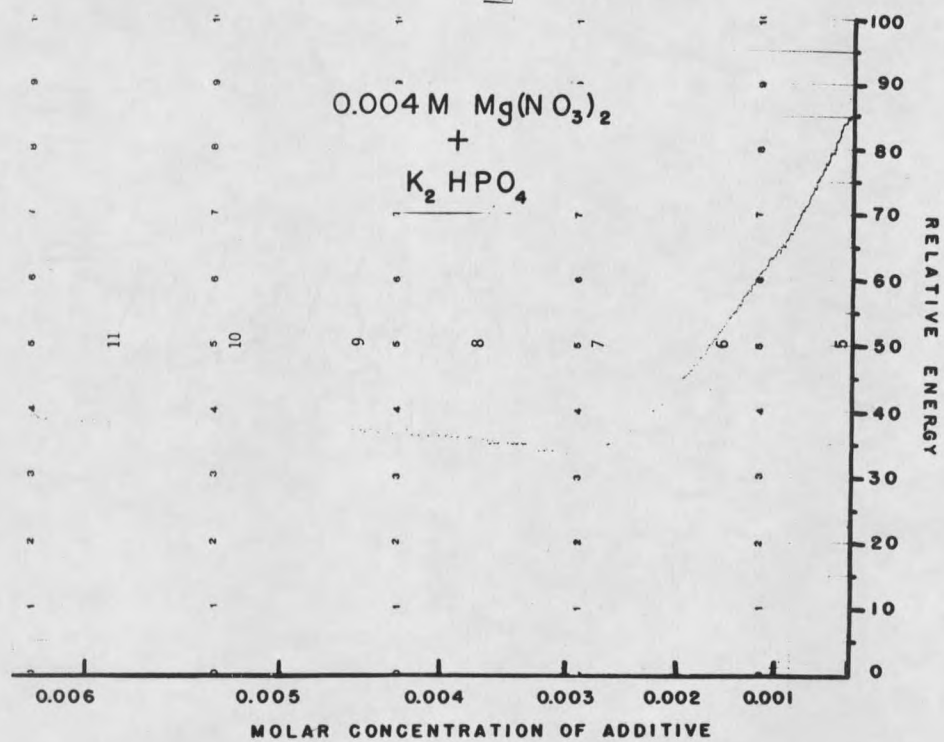


FIGURE 17

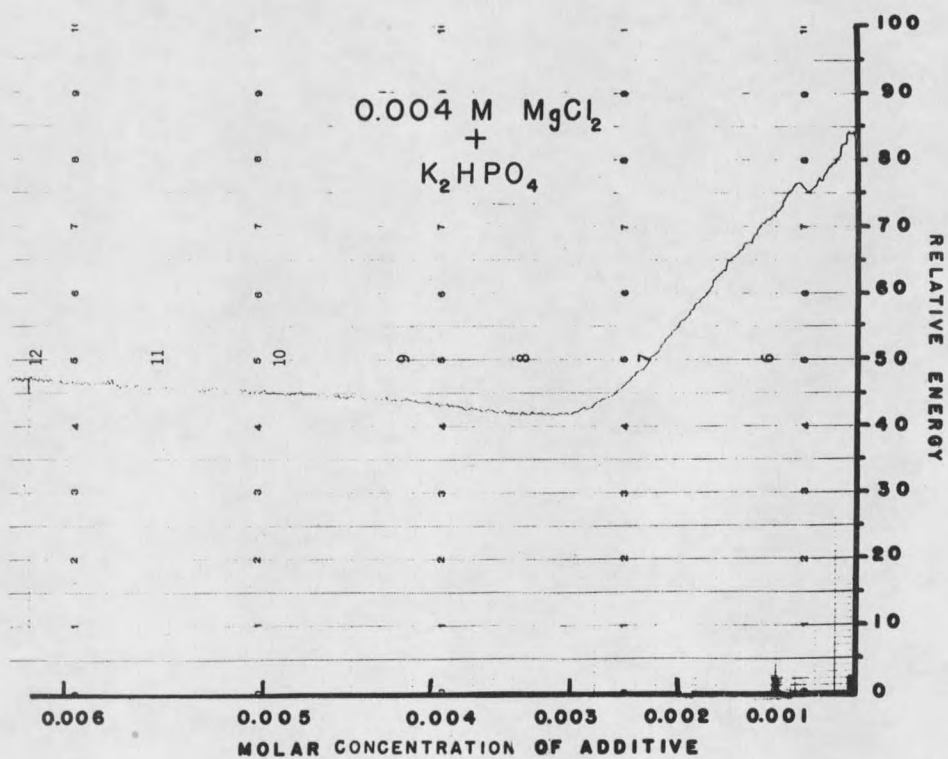


FIGURE 18

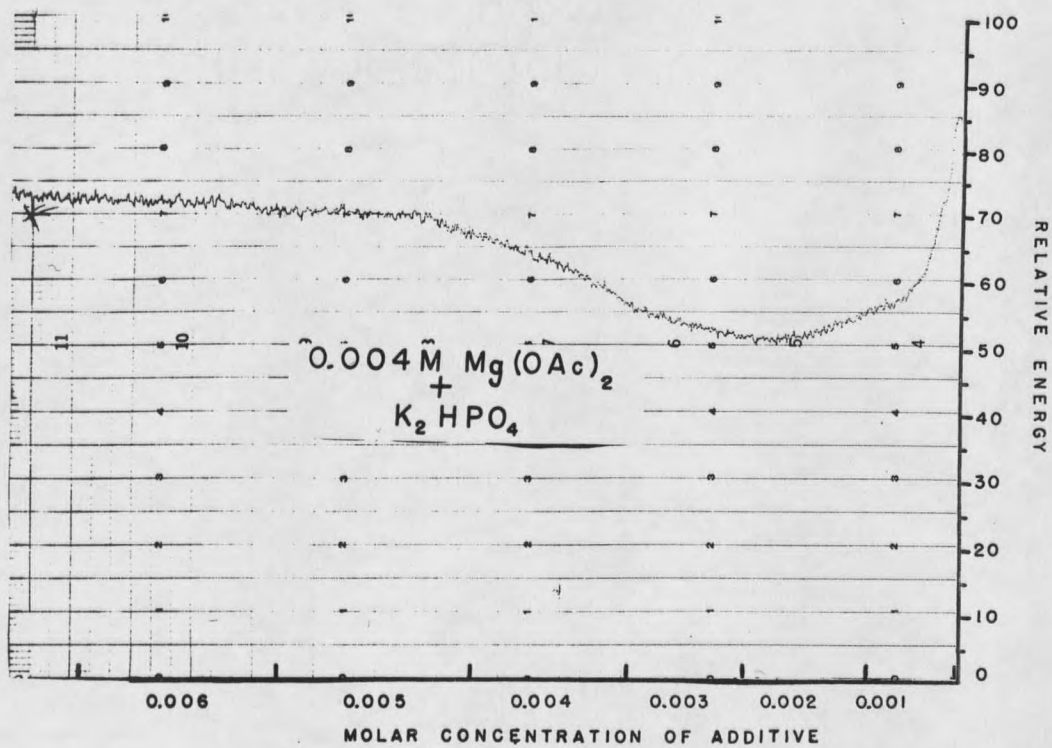


FIGURE 19

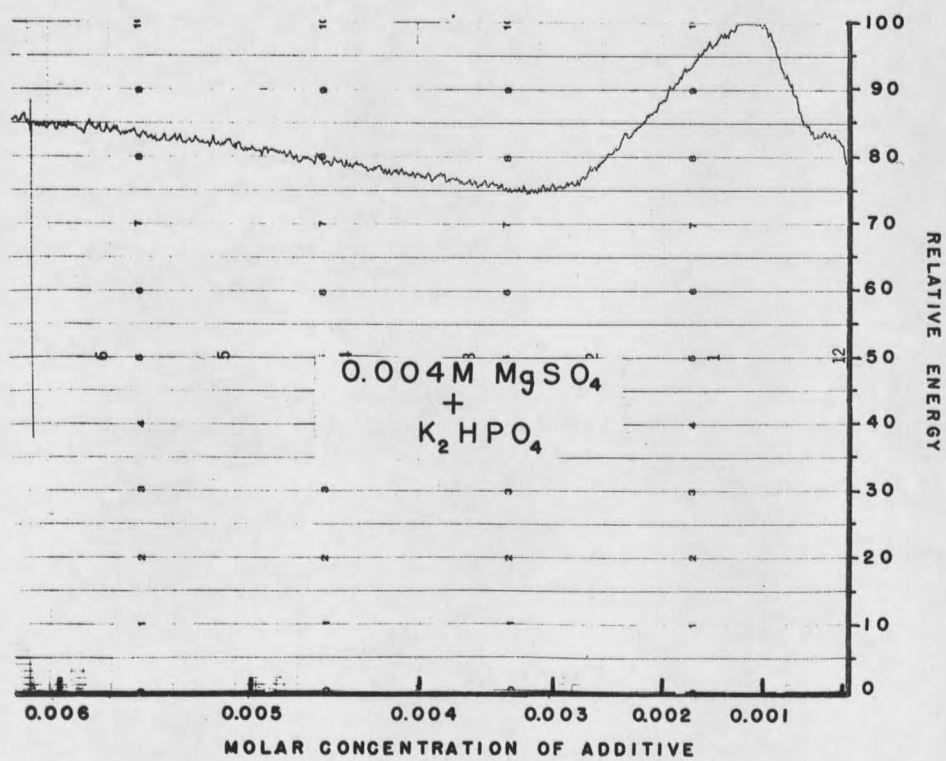


FIGURE 20

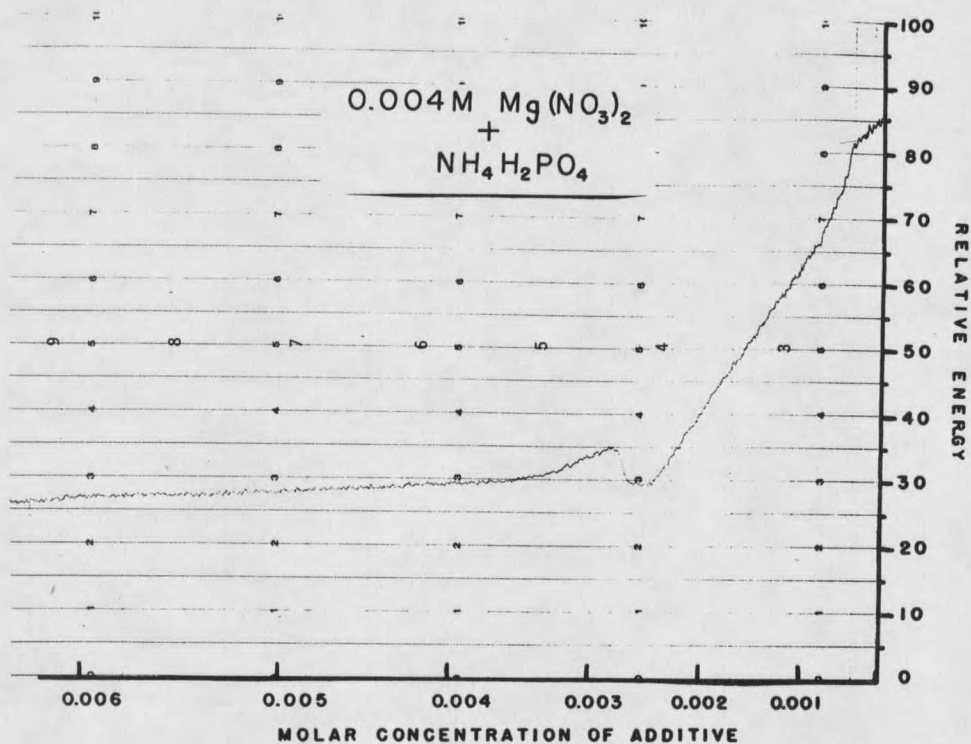


FIGURE 21

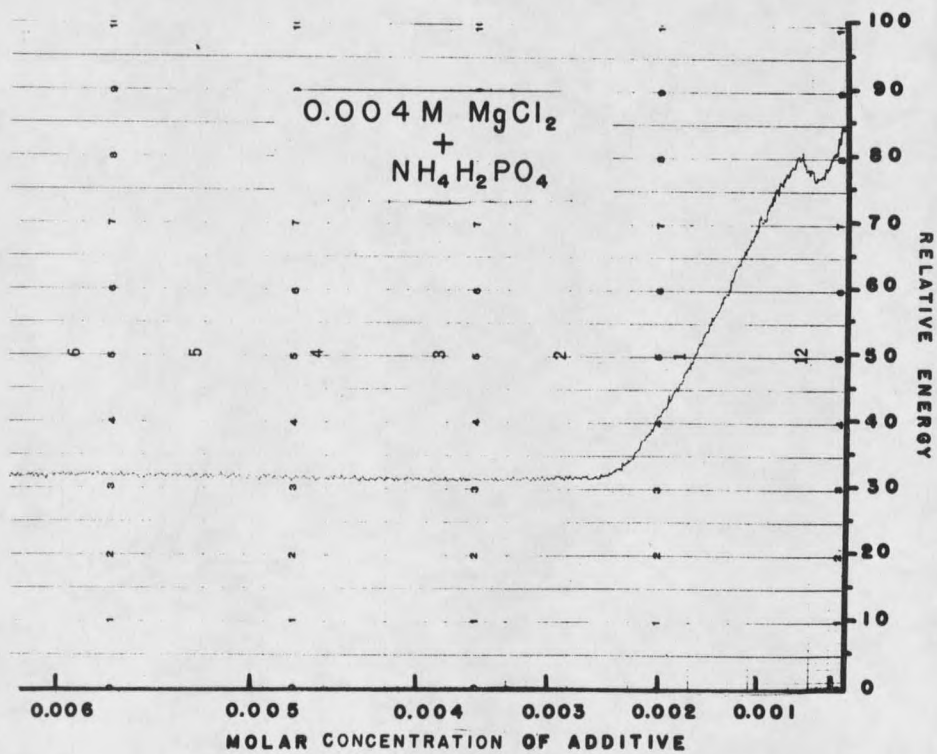


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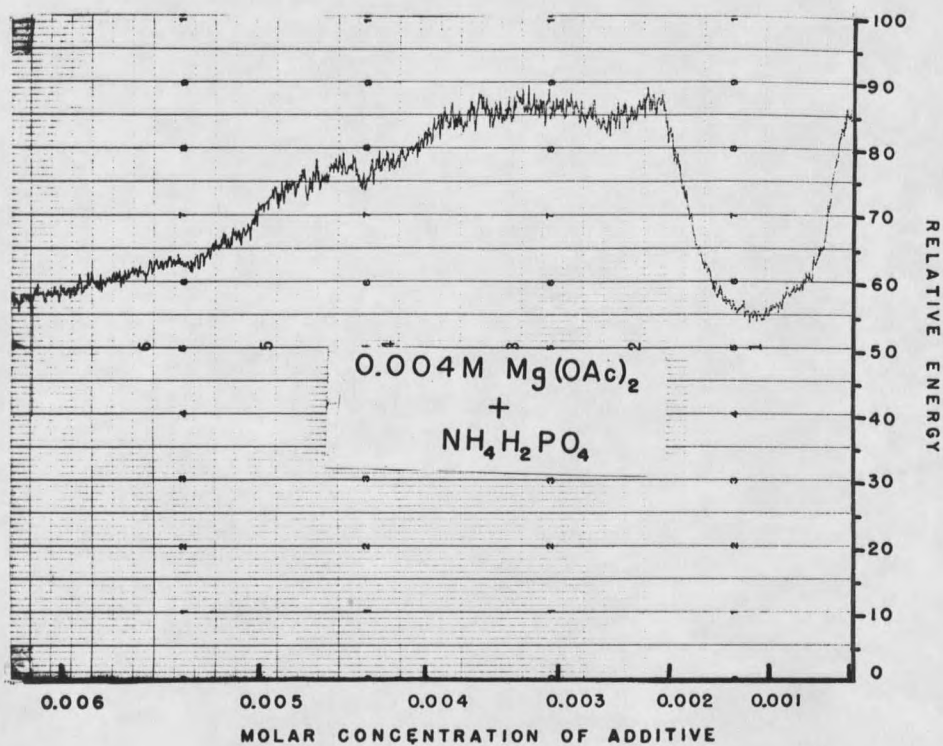


FIGURE 23

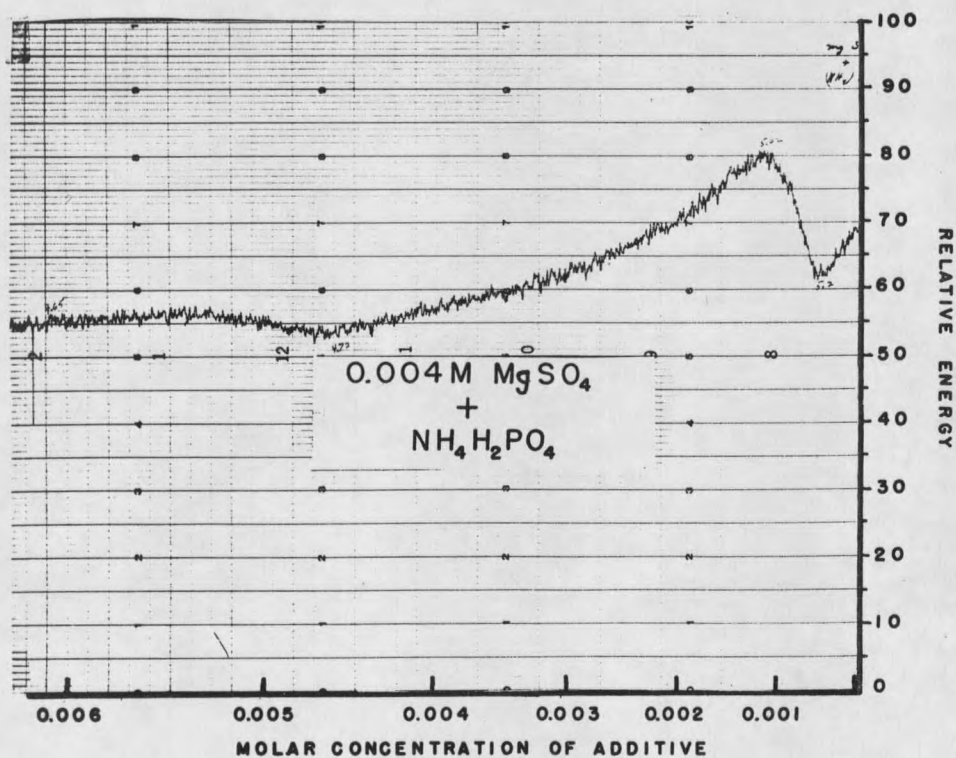


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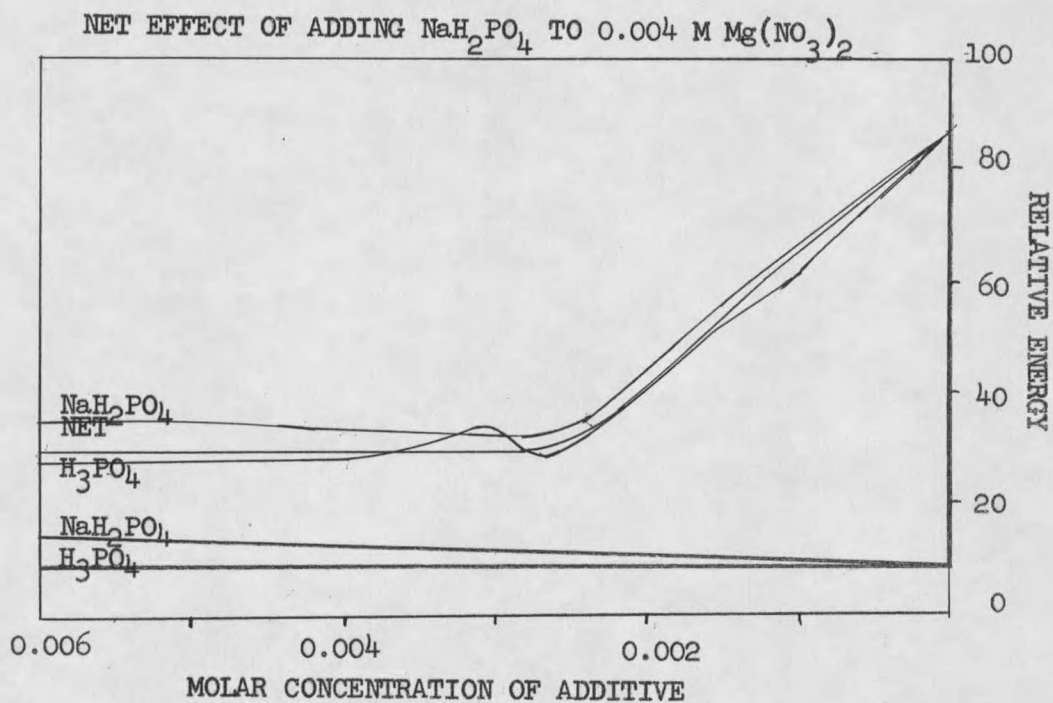


FIGURE 25

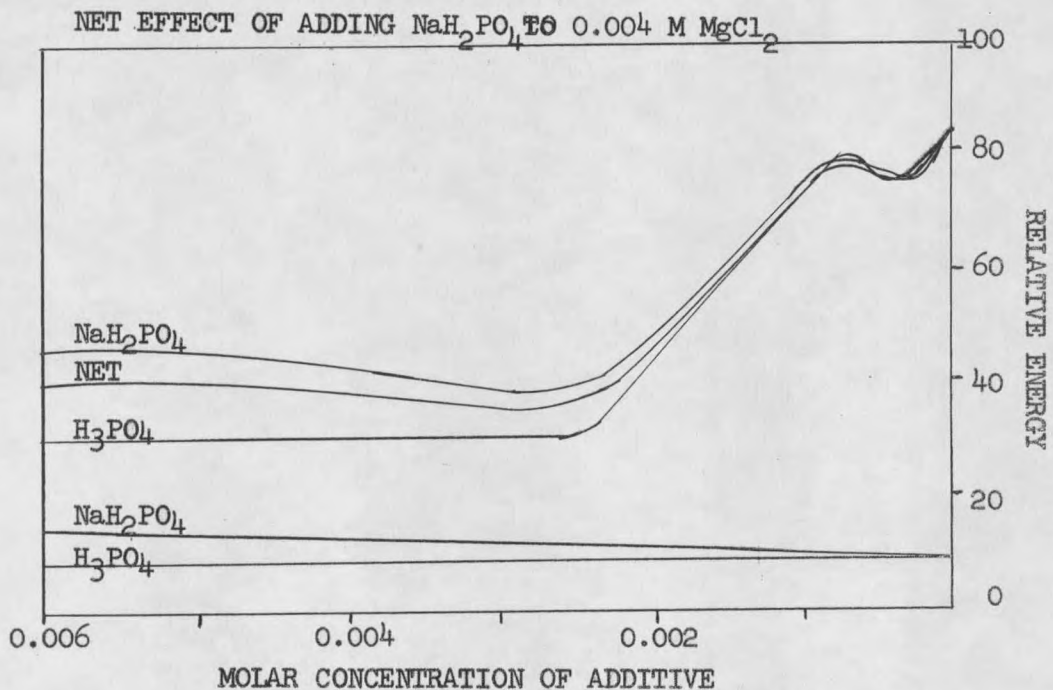
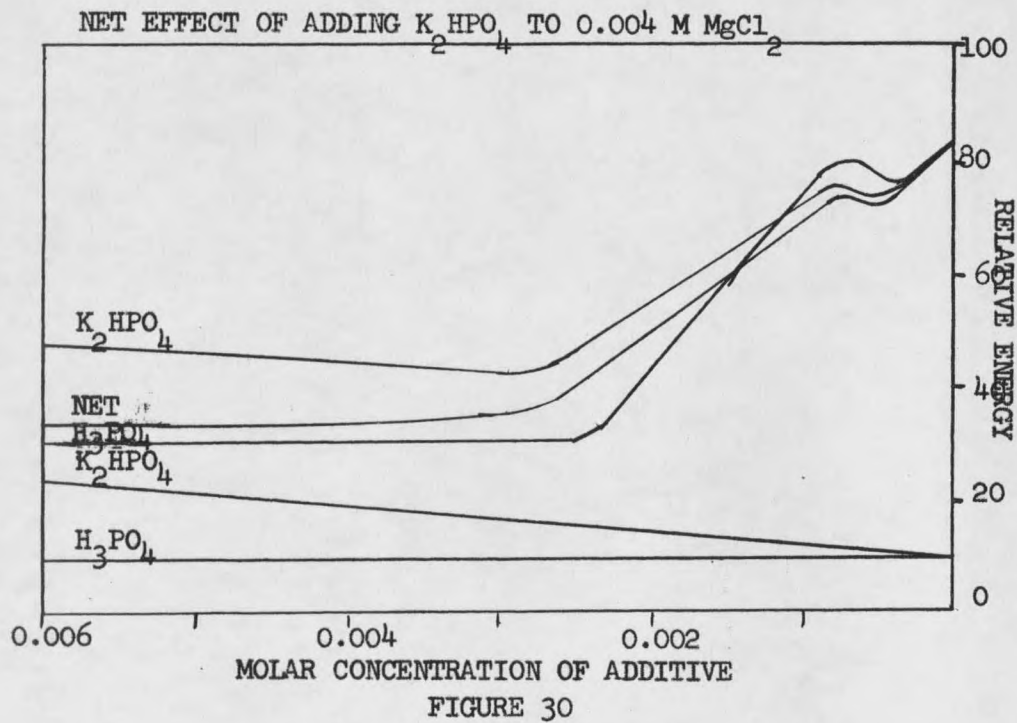
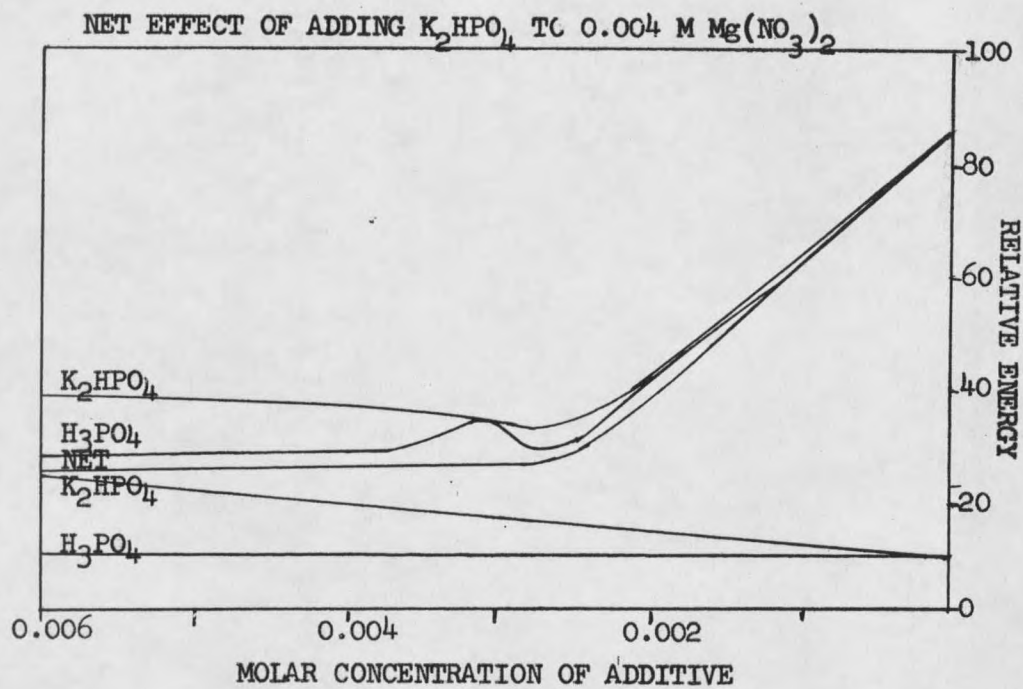


FIGURE 26



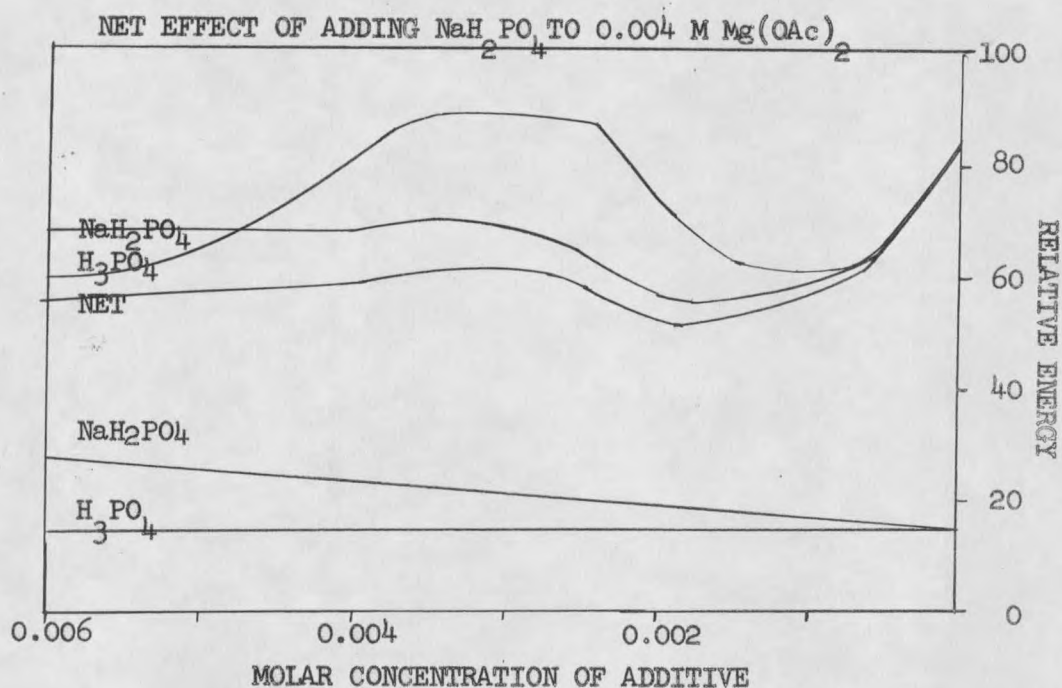


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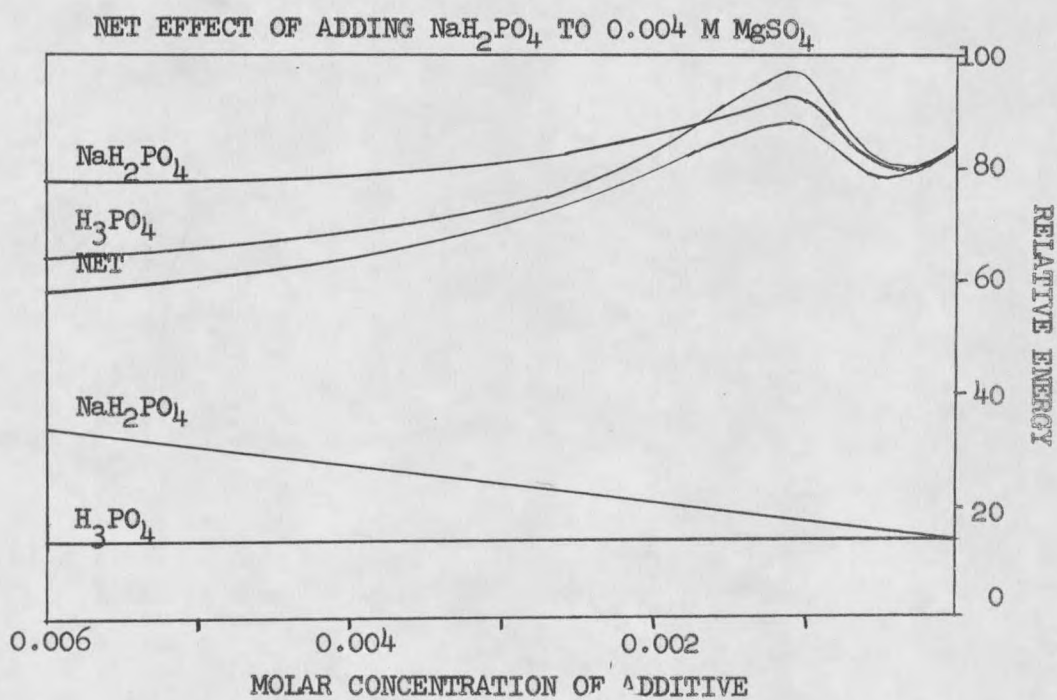


FIGURE 28

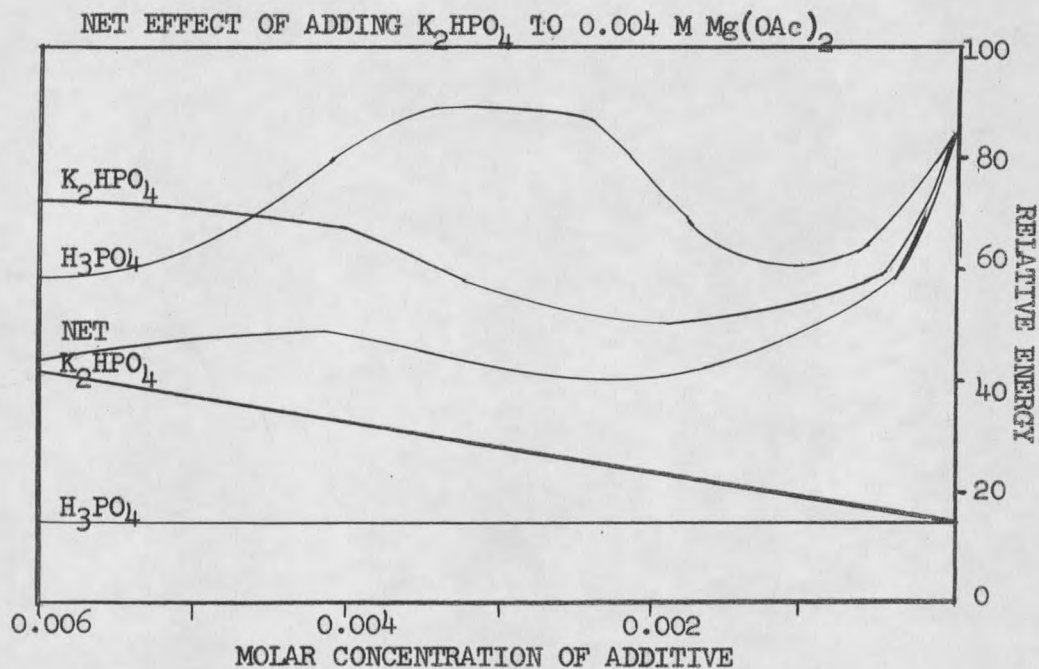


FIGURE 31

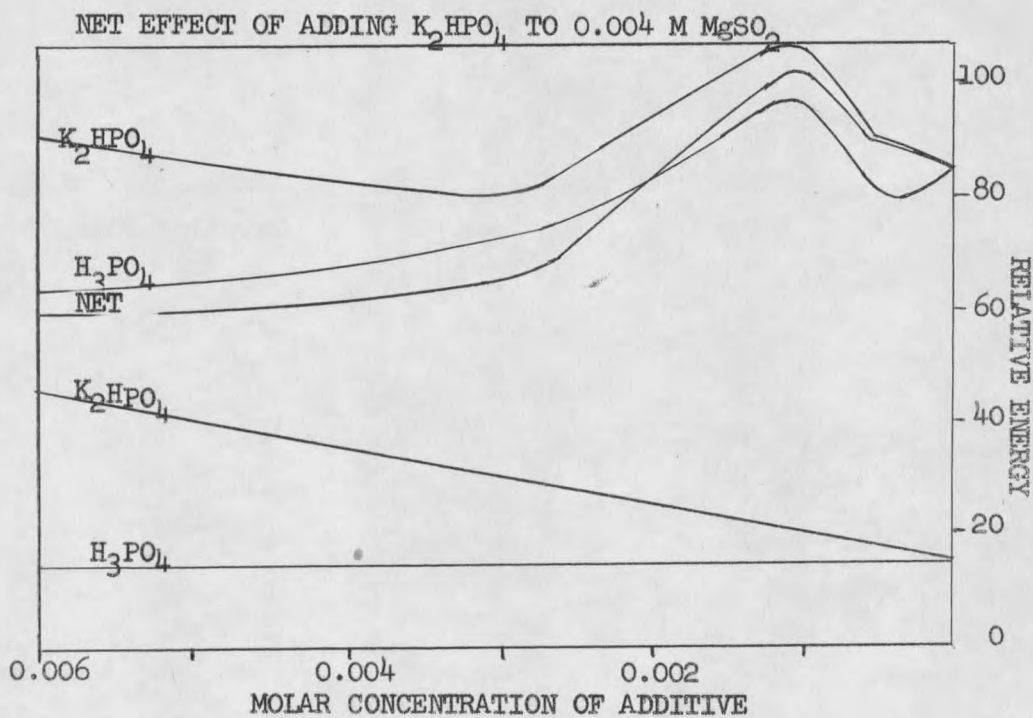


FIGURE 32

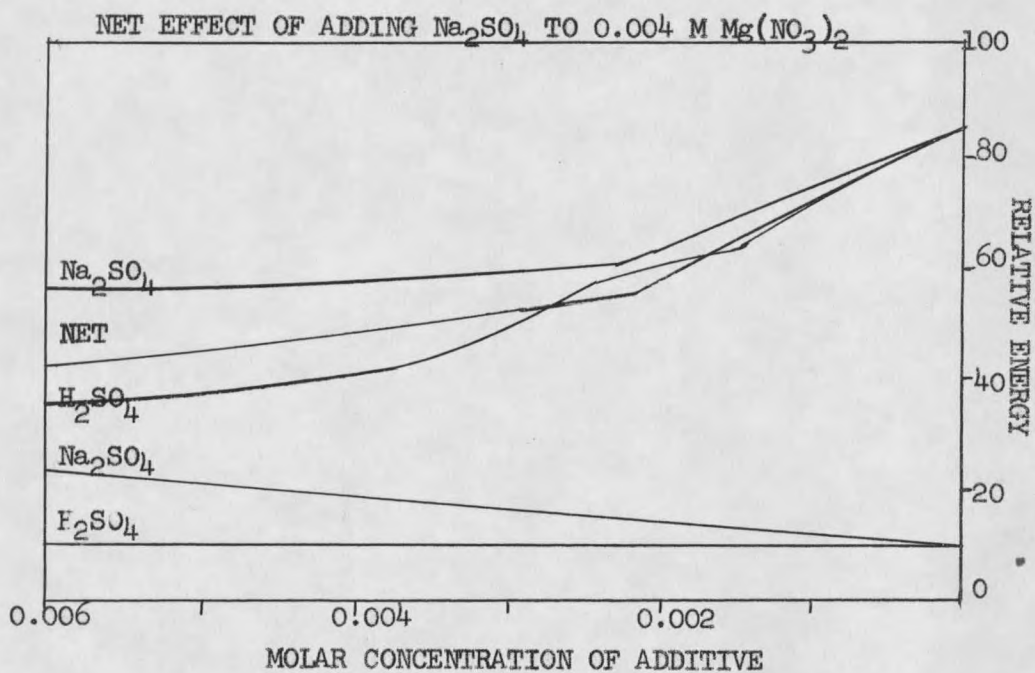


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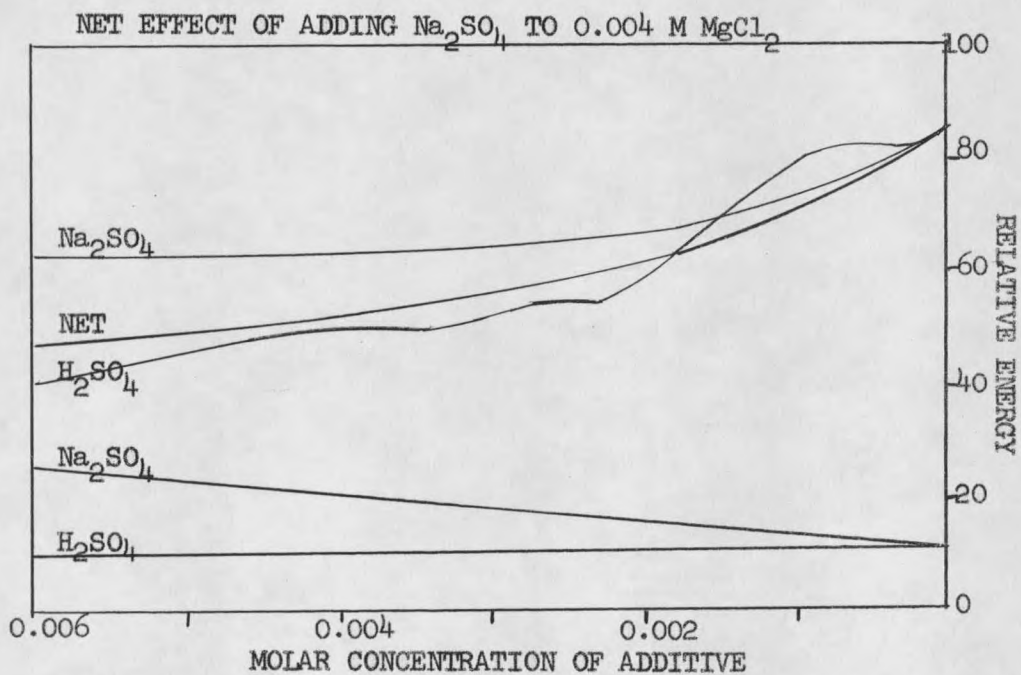


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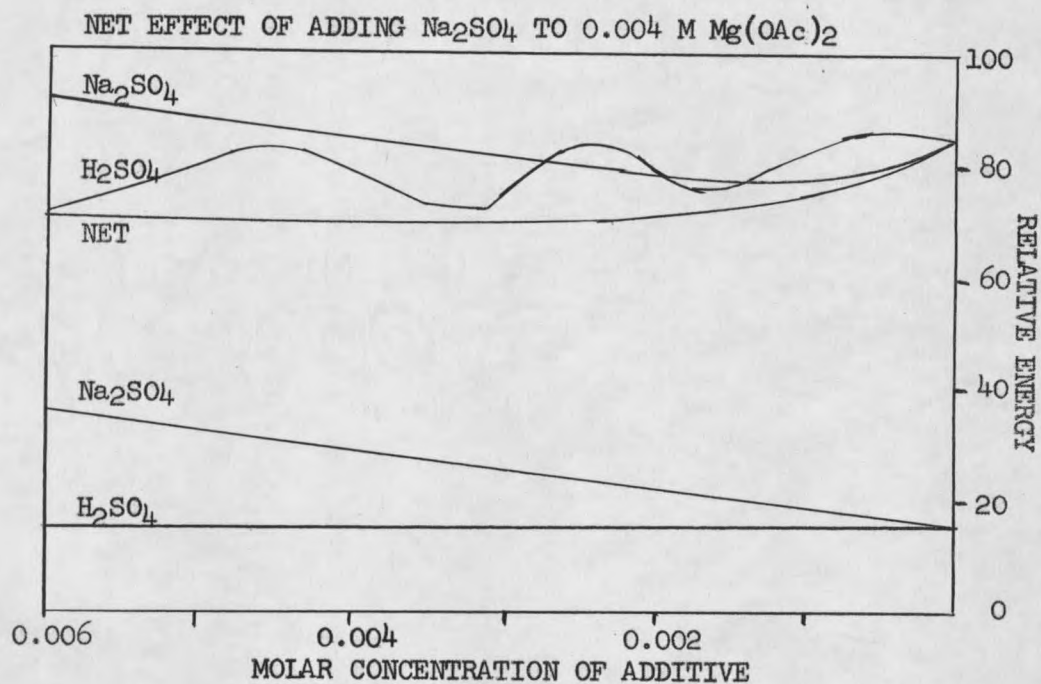


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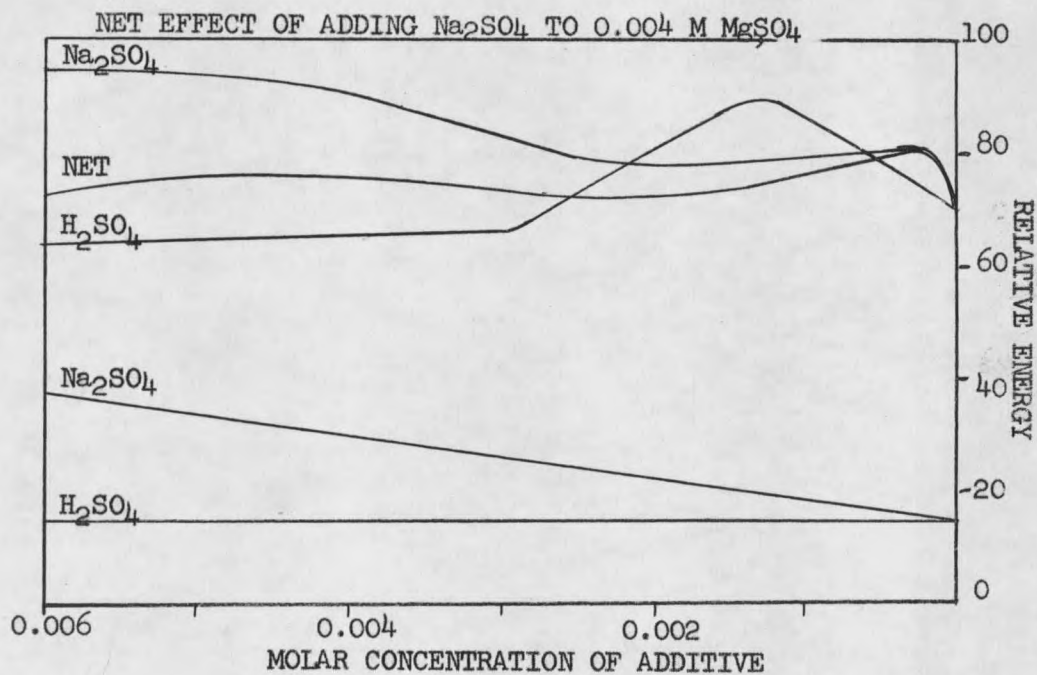


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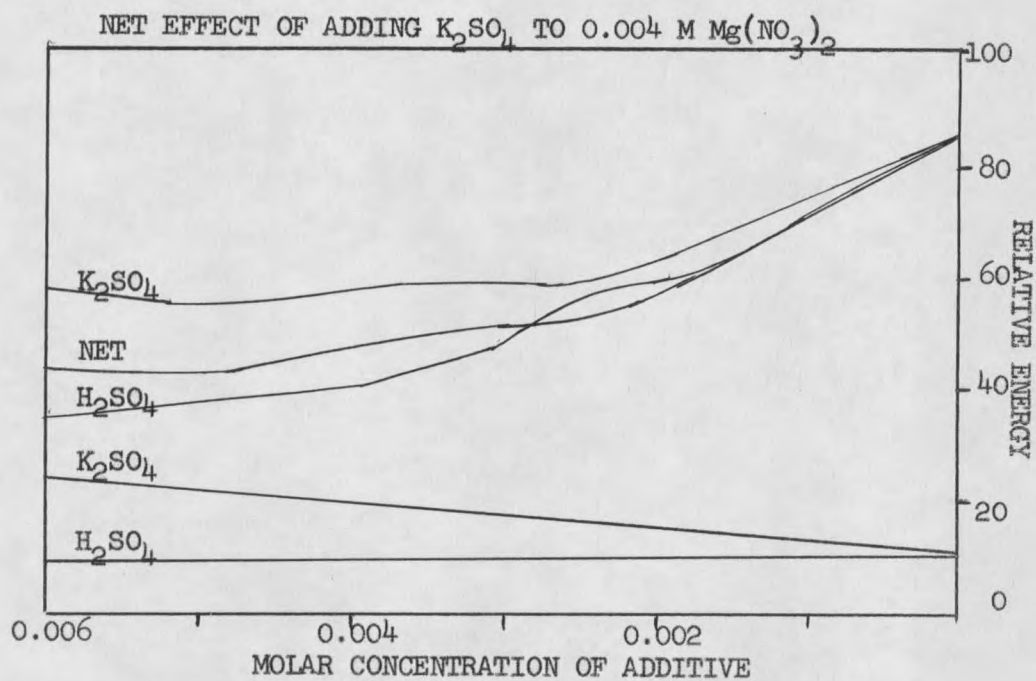


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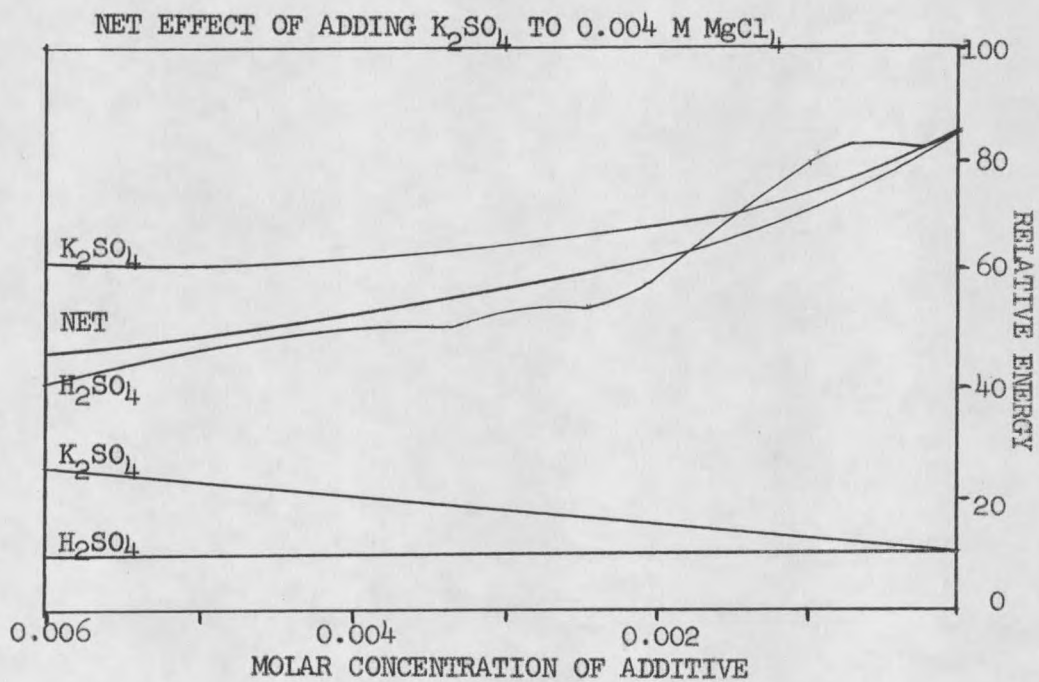
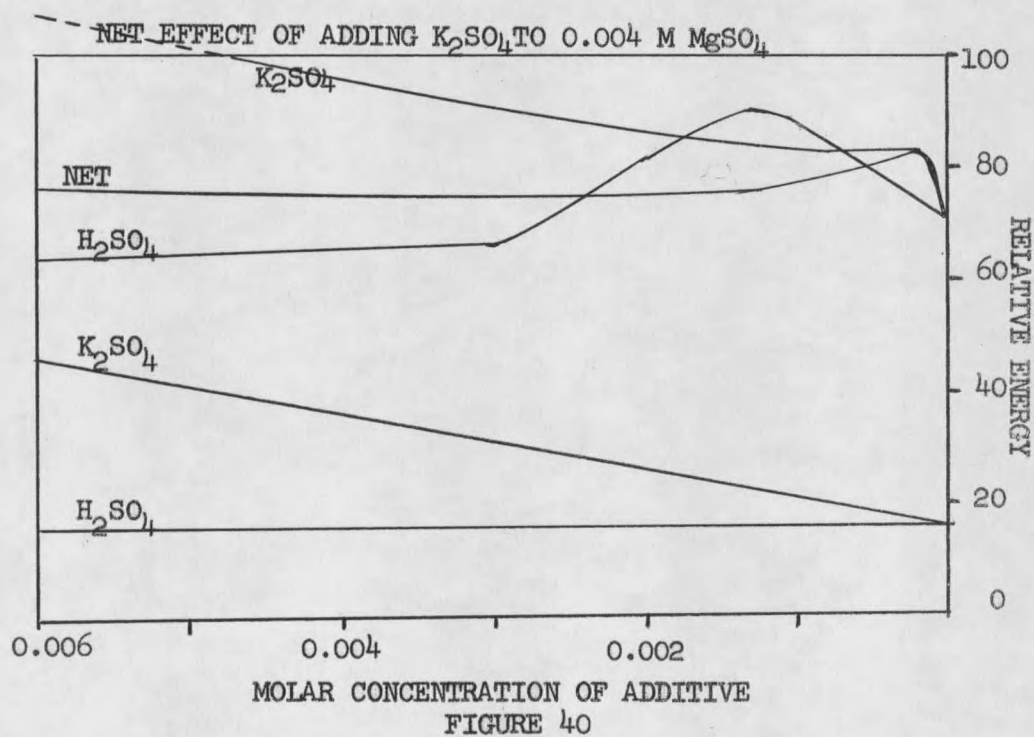
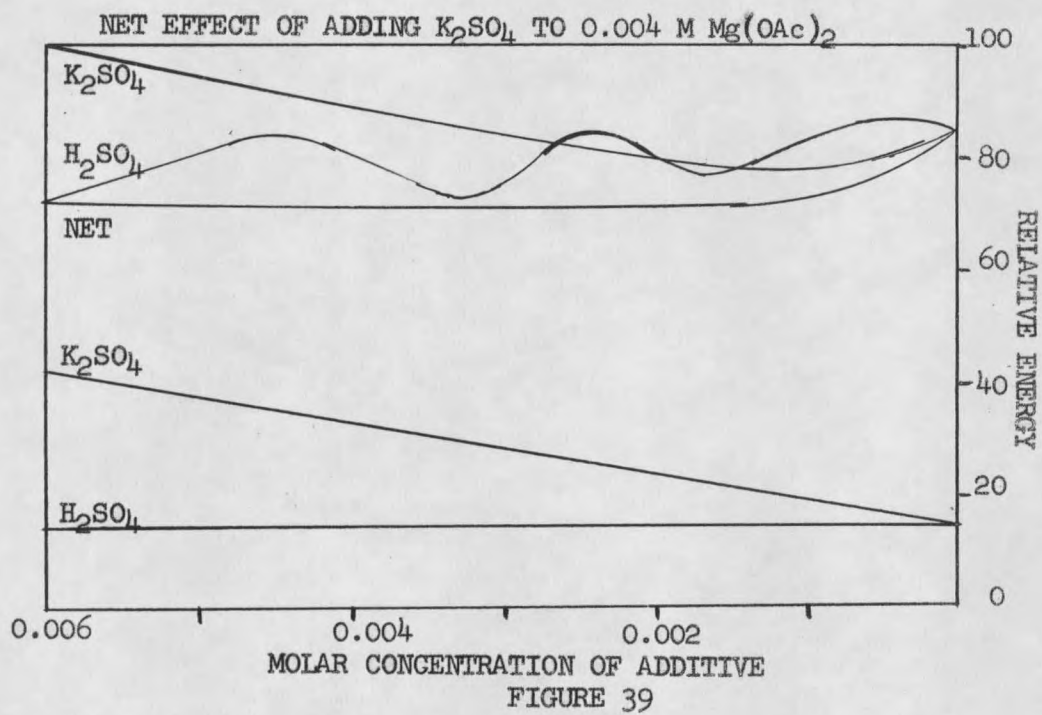


FIGURE 38



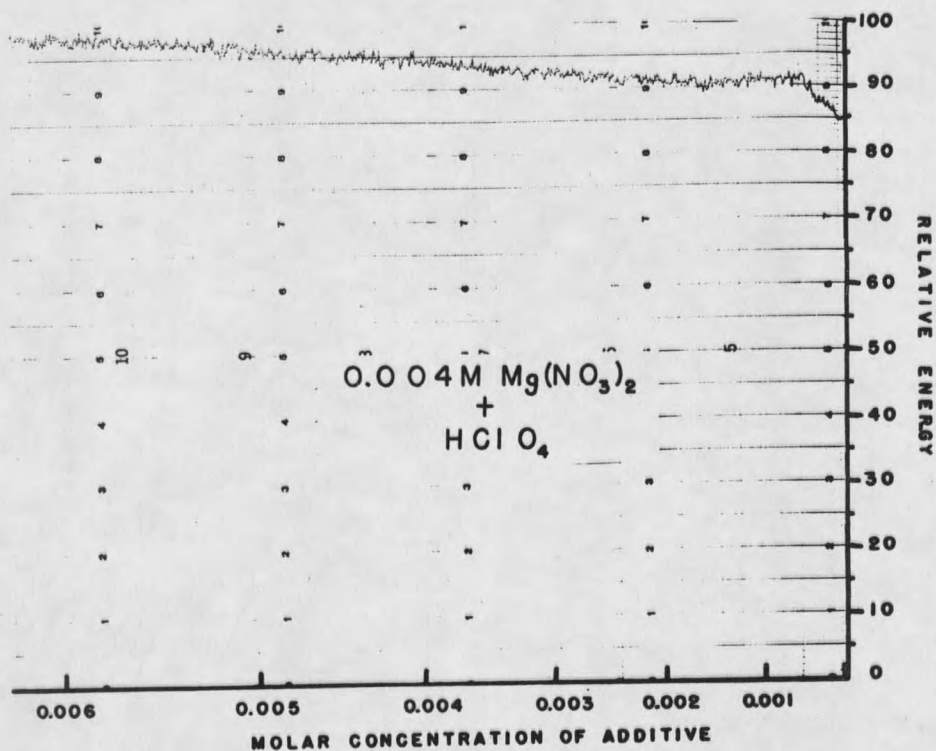


FIGURE 41

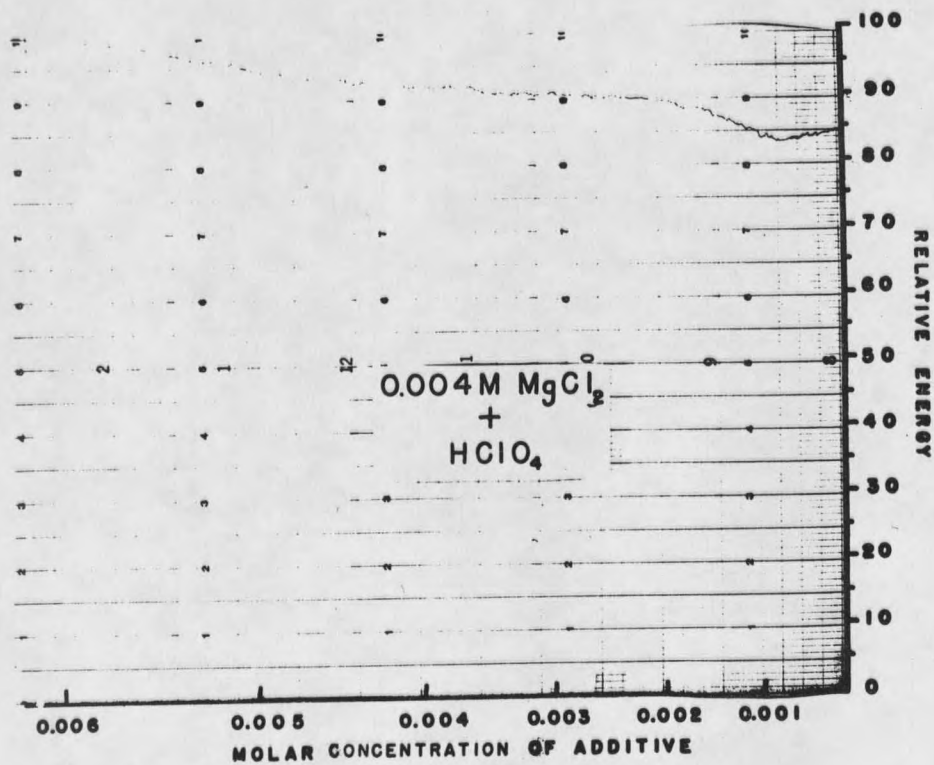


FIGURE 42

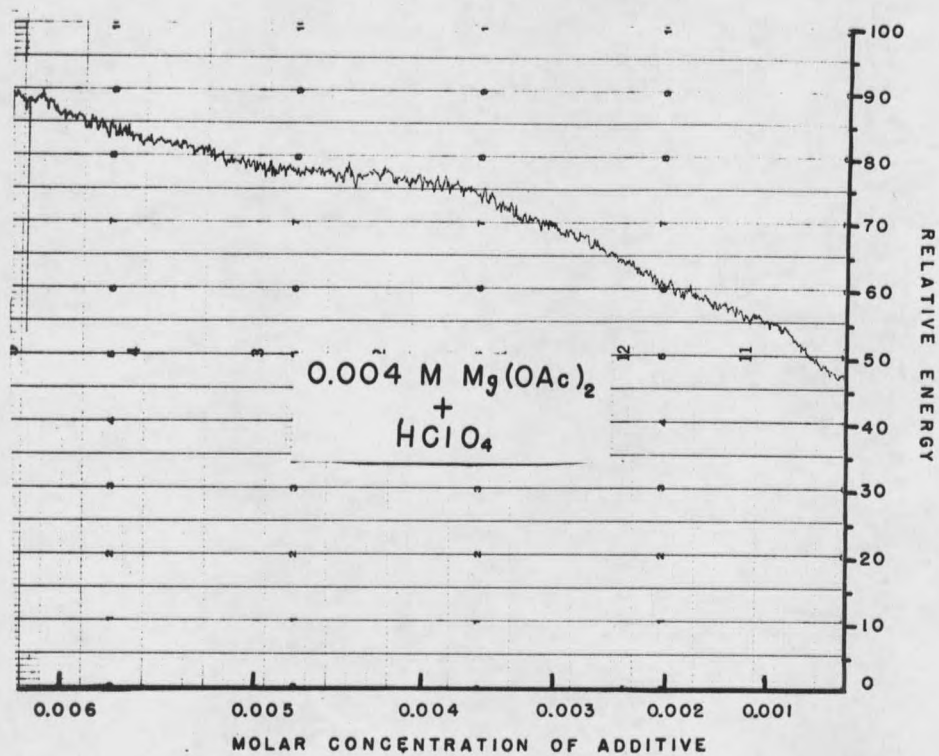


FIGURE 43

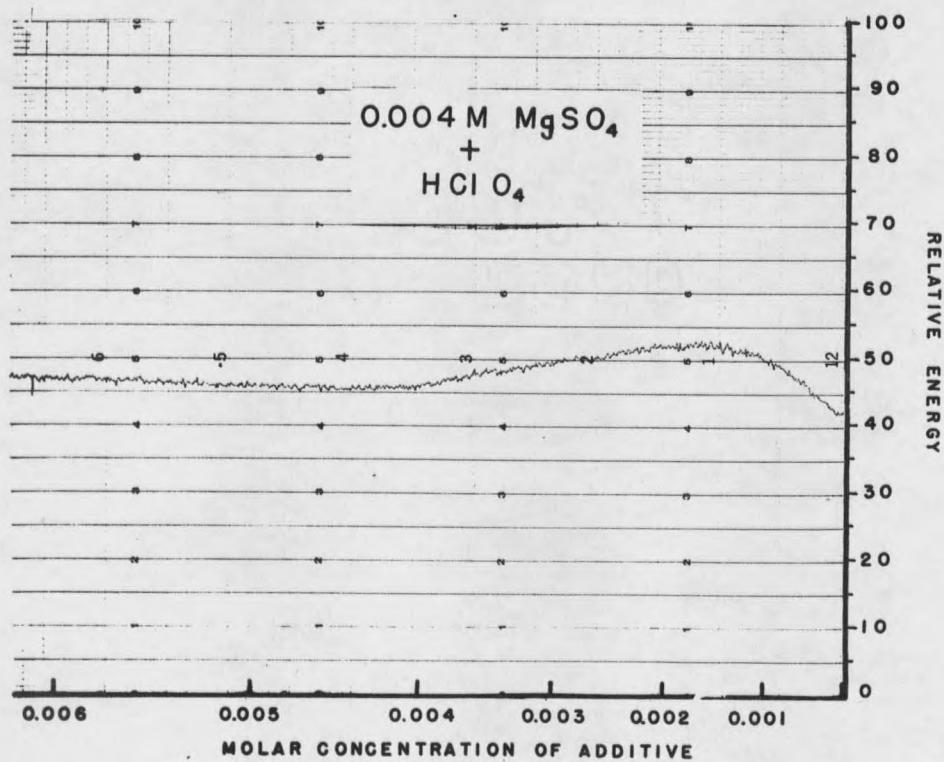


FIGURE 44

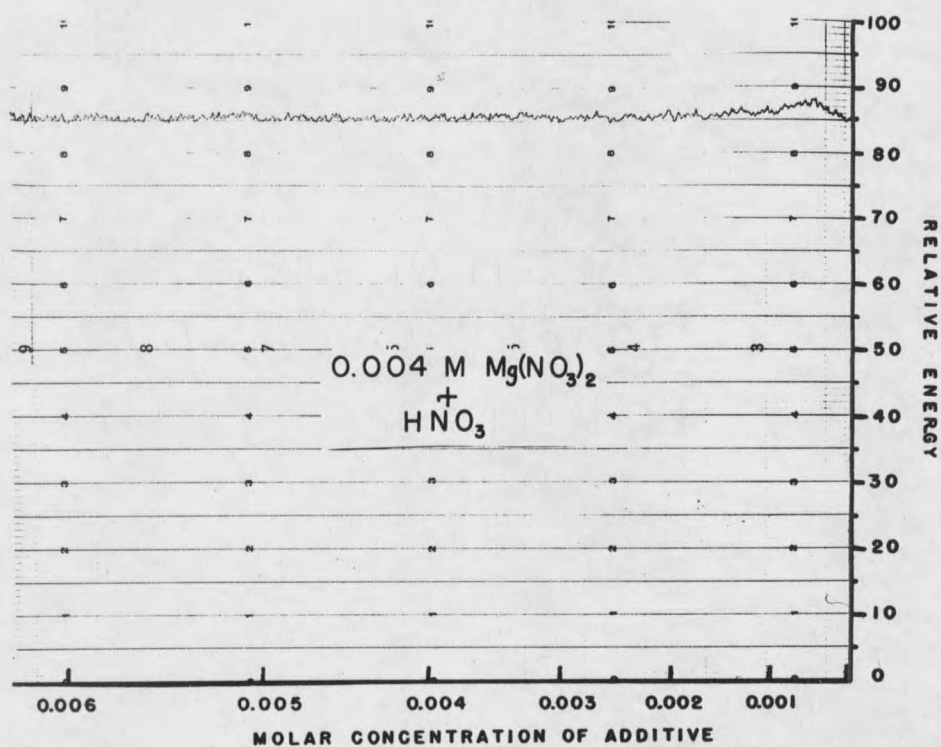


FIGURE 45

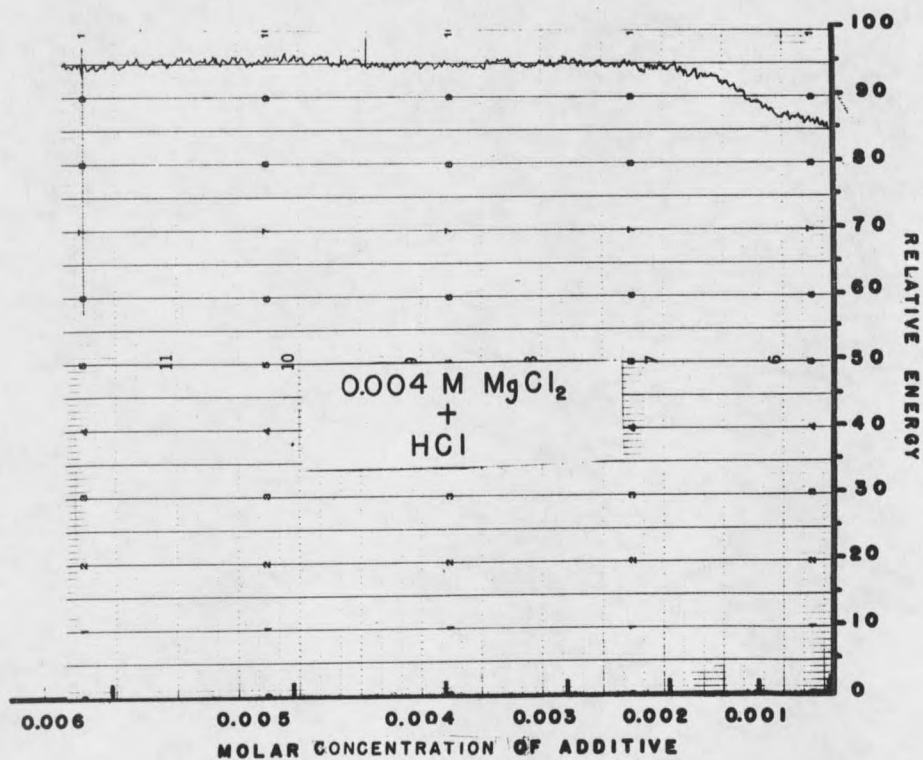


FIGURE 46

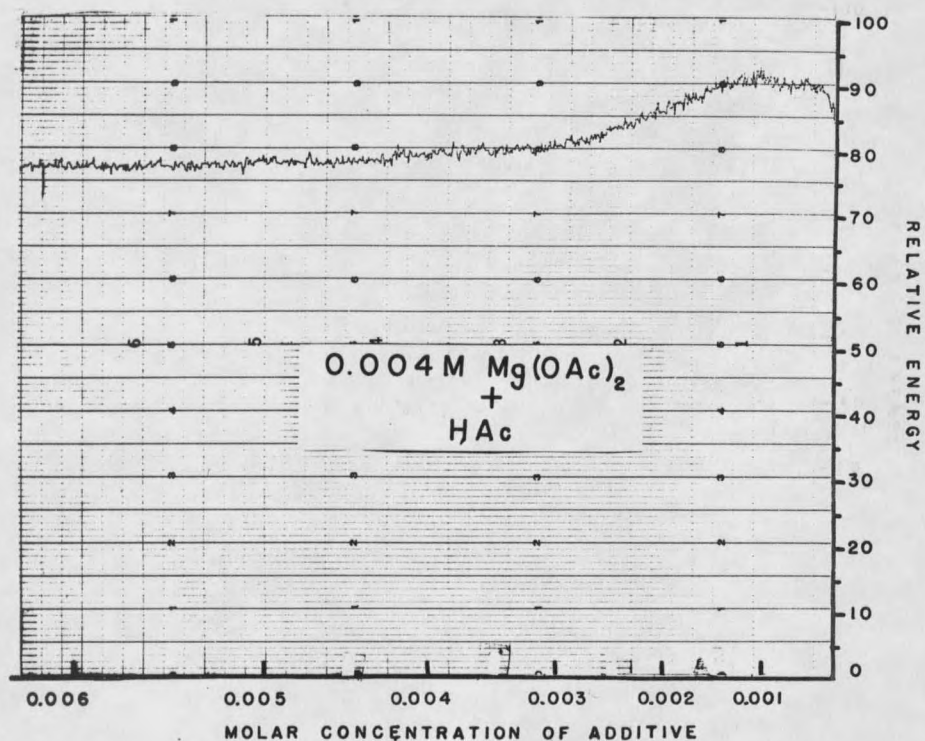


FIGURE 47

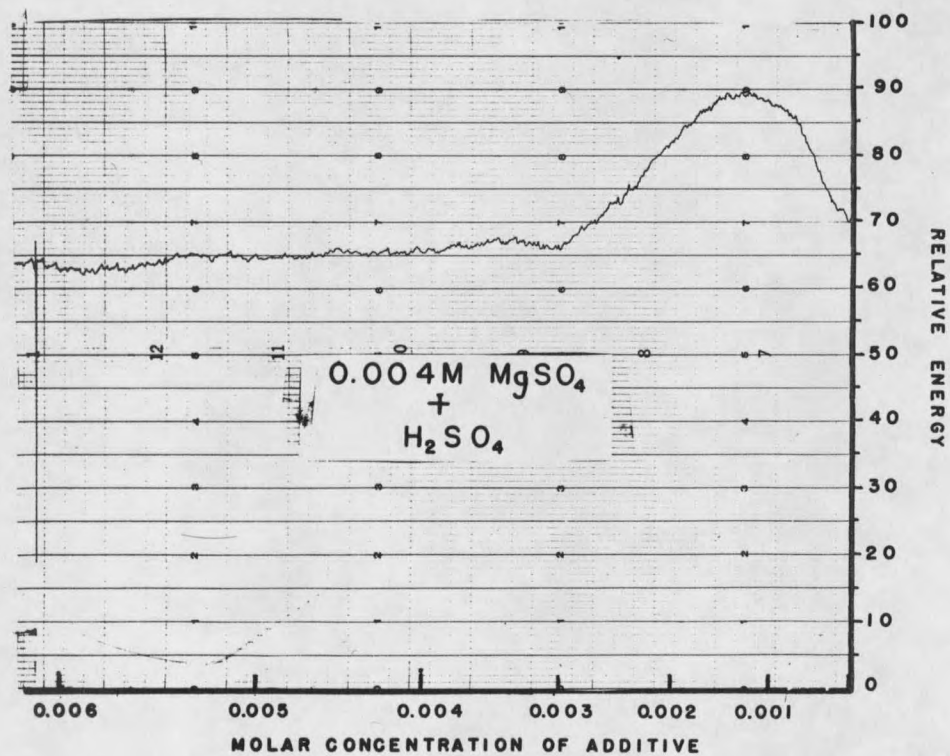


FIGURE 48

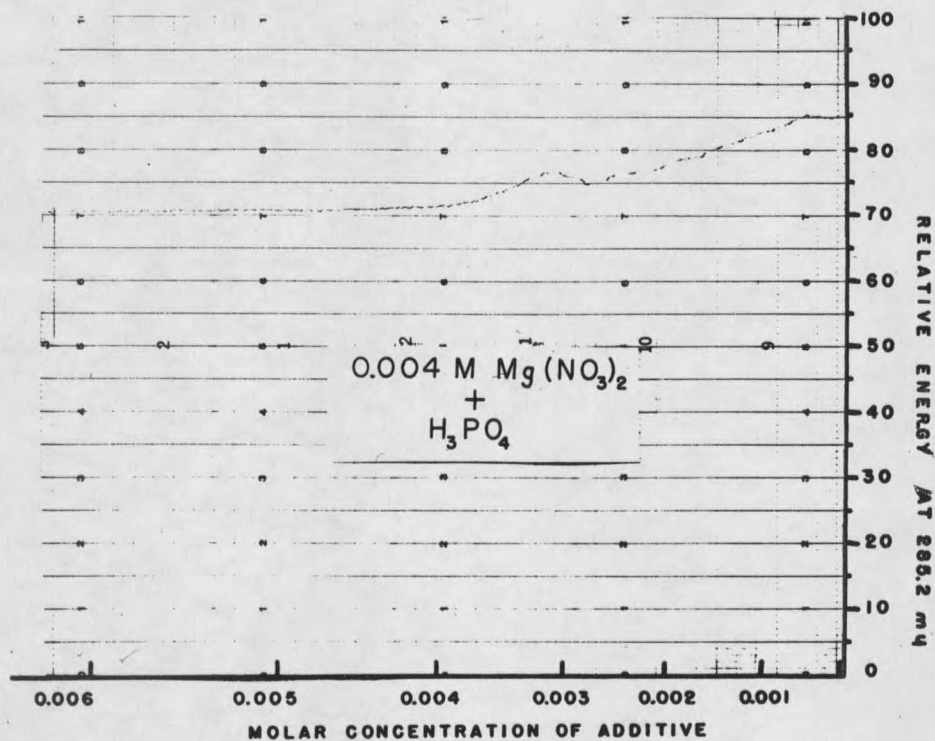


FIGURE 49

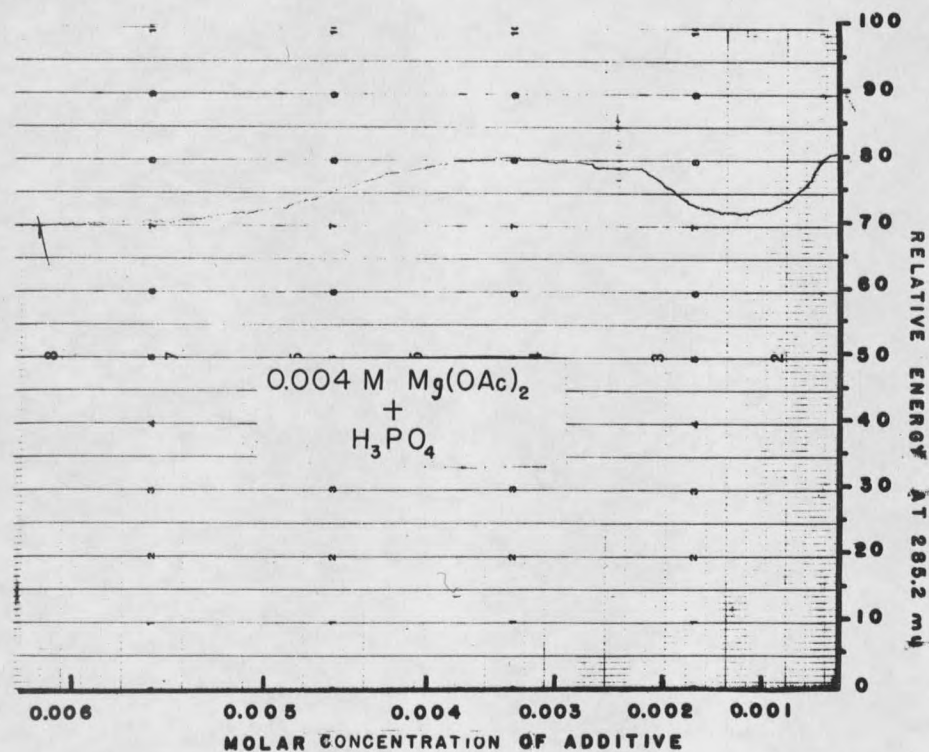


FIGURE 50

The difference in results for the addition of hydrochloric acid was disturbing, not because the difference could not be explained but because of the inference drawn from the results. The difference was quite probably due to the difference in magnesium chloride standards used in the two investigations. The standard used by Anderson, prepared as it was by reacting magnesium ribbon with hydrochloric acid and then driving off the excess acid by evaporation, would appear to have had a greater chance of being contaminated than the one used in the present investigation. One quite possible contaminant would appear to have been hydrochloric acid. Anderson had drawn the conclusion, from his results, that the hydrogen ion had no significant effect on the emission intensity of magnesium. Judging from information presented in this investigation it would appear that Anderson's conclusion could be questioned. In addition to the effects noted when hydrochloric acid was added to magnesium chloride, figure 46; the effects of adding nitric acid to magnesium nitrate, figure 45; acetic acid to magnesium acetate, figure 47; and sulfuric acid to magnesium sulfate, figure 48, all show a rapid moderate increase in emission intensity. It was found that the addition of sodium chloride to magnesium chloride would produce an identical rapid moderate increase in emission intensity as was noted when hydrochloric acid was added. From these results it would appear that no definite conclusion as to hydrogen ions affecting magnesium emission intensity can be drawn.

The investigation of comparative value of the various wave lengths used for measuring magnesium emission intensity has been discussed in some detail in the experimental section. It was pointed out that, even

when magnesium emission is depressed to a minimum by anion effects, the emission to background ratio is most favorable at the 371 mu wave length. It was pointed out that anion effects appeared to be less pronounced at the 285.2 mu wave length than at the 371 mu wave length. A close investigation showed this to be true, and that depressing effects are similar in detail at both wave lengths is evidenced by comparing figures 9 and 11 with figures 49 and 50. Numerous other comparisons of detail were made with results showing uniform agreement. From this data it is evident that the recorded relative energy is more intense at 371 mu than at the other principal wave lengths.

Emission by sodium and potassium at 371 mu can be compensated for in analytical work by adding these elements to the standards in approximately equal amounts as are found in the samples. When the concentration of these elements, or other enhancing elements, is comparatively high they will alter the emission to background ratio at 371 mu. If measurements were made at 285.2 mu this difficulty may be avoided in some instances.

Previous workers have shown that a close relationship exists between the effects of anions on the emission intensity of calcium and magnesium. Workers with both elements have observed depression curves with single inflection points. Molar ratios of calcium to phosphorus or sulfate and magnesium to phosphate or sulfate were shown to be constant and independent of concentration at the point at which complete depression was reached. This led the workers to suggest that the observed effects were due to the formation of calcium or magnesium

compounds as the solutions evaporated in the flame and the emission intensity was related to the ease of forming the oxides from the initial compound formed. To demonstrate, they assume that the chlorides will be more easily oxidized than the phosphates and since the phosphates are less soluble they will form first as solutions evaporate in the flame, thus, as increments of phosphoric acid were added to calcium or magnesium chloride solutions the emission intensity would decrease until all of the calcium or magnesium came down as a phosphate.

In the present investigation single inflection point curves for the addition of phosphoric and sulfuric acids to magnesium solutions were not observed. This indicated that the suggested cause of depression was either wrong or needed refinement. A possible refinement that could explain at least part of the irregularities of the curves as shown in this investigation would be that the predominant anion form may change as varied increments of the acids are added. For instance, as phosphoric acid is added the shift in predominant anion would be from $\text{HPO}_4^{=}$ to $\text{H}_2\text{PO}_4^{=}$ at normal temperatures. This could result in the formation of different magnesium compounds which would require different quantities of energy to convert them to oxides and thus produce inflections in the emission intensity depression curves as noted. Under more normal conditions the compounds formed could be quite accurately calculated but what happens in a droplet of solution that suddenly finds its-self in an oxygen-hydrogen flame?

To check the possibility of the shift in ionic form, various phosphate and sulfate salt solutions were used as additives to minimize the

possible shift in anion form due to a change in hydrogen ion concentration. It was believed that a disappearance or shift in position of an inflection in the depression curve from that noted for the addition of the acid could be interpreted as supporting evidence for the suggested reason for observed results when phosphoric and sulfuric acids were added. The addition of sodium and potassium phosphate salt solutions to the various magnesium standards did result in the disappearance of several inflection points in the emission intensity depression curves as produced by the addition of phosphoric acid. For example, in figure 25 the inflections shown in the H_3PO_4 curve at 0.003 M is absent in the Na_2HPO_4 net curve. A similar disappearance of inflections as produced by the addition of sulfuric acid was noted when sodium and potassium sulfate solutions were added to the magnesium standards.

It is felt that though these results are inconclusive they do support the suggested reason for the observed results of adding phosphoric and sulfuric acids. The fact that high temperatures and extremely rapid changes of physical environment are involved makes interpretation of the results quite difficult.

V ACKNOWLEDGEMENTS

The author wishes to take this opportunity to express his appreciation and thanks to the administration and staff of the chemistry station for facilities made available and suggestions offered during the investigation. Suggestions made by chemistry department staff members and fellow graduate students were also appreciated. Special thanks are extended to Graeme Baker and Dr. Ralph Olsen for their patience and suggestions in compiling this report.

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