

with sodium acetate, whose hydrogen-ion concentration is  $3.2 \times 10^{-8}$  in a tenth molar solution, it would assume a position much nearer the strong nitric acid than the weak acetic acid. Such an approximation would place it near sulfuric acid but below it.

### Summary

1. The presence of disodium dihydrogen pyrophosphate is given as an explanation for the acidity of solutions of "Graham's salt" and solutions of other sodium metaphosphates prepared by heating monosodium orthophosphate when they are not purified by repeated crystallizations from water.

2. The monometaphosphoric acid is near but below sulfuric acid with respect to its activity.

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## CALCIUM NITRATE. III. HEATS OF HYDRATION AND OF SOLUTION OF THE BINARY SYSTEM CALCIUM NITRATE-WATER

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By means of well-known thermodynamic principles, heats of hydration of salts can be calculated from vapor pressure-temperature data. The system calcium nitrate-water lends itself admirably to an investigation of these relationships since the salt crystallizes from water in four forms—the tetrahydrate, the trihydrate, the dihydrate and the anhydride, according to the concentration of the solution and other conditions. In a previous article,<sup>1</sup> a temperature-composition diagram was presented showing that each of these crystalline forms can exist in a metastable equilibrium with what is ordinarily called a supersaturated solution. In reality they are saturated solutions of the metastable crystals. In a second article,<sup>2</sup> temperature-vapor pressure data for the mixture of crystals of this system were presented. It was shown that equilibrium vapor pressures could be measured not only for the stable eutectic mixtures tetrahydrate-trihydrate, trihydrate-dihydrate, and dihydrate-anhydride, but also for the metastable eutectic mixtures tetrahydrate-dihydrate and tetrahydrate-anhydride.

Fragmentary data are given in "International Critical Tables" for the experimental heats of this system. In order to compare the heats calculated from vapor pressure measurements with experimental data, it seemed advisable to make accurate heat measurements for the reactions

<sup>1</sup> Ewing, Krey, Law and Lang, *THIS JOURNAL*, **49**, 1958 (1927).

<sup>2</sup> Ewing, *ibid.*, **49**, 1963 (1927).

involved, employing modern calorimetric methods. The heats of solution of the anhydride, the dihydrate, the trihydrate and the tetrahydrate have been measured. From these data, one can calculate the heat of hydration from any lower hydrate to any higher one.

Similar measurements have been made also for the binary system strontium nitrate-water as vapor pressure-temperature data for this system are now being obtained in this Laboratory.

The general procedure for measuring the heats of solution was to introduce the solute into water and measure the temperature change under adiabatic conditions. This temperature change was then reproduced by means of electrical energy, and the electrical energy necessary to reproduce these changes was equated to the heat of solution. If due precautions are taken to have all changes in the system the same during the electric heating and the chemical heating, this method practically eliminates corrections for heats due to stirring, evaporation, electrical stray fields due to the bath heating current, etc. Precautions were taken to minimize any effect which might cause error, however, in order to make the changes which must be compensated for as small as possible.

### Experimental

The adiabatic calorimeter used in making these heat measurements contains features described by Cohen, Moesveld and Helderman,<sup>3</sup> Daniels,<sup>4</sup> and others. Its details are illustrated in Fig. 1.

The outer can was made of copper. The heavy copper cover was attached to the can by means of the ground brass joint, G, which was well coated with rubber desiccator grease; after closing, it was sealed with universal wax. No sign of leakage was ever detected. A, B and C are copper chimneys lined with hard rubber tubes. Also the stems of the breaking devices and of the heater-stirrer were made of hard rubber. Four chimneys are not shown in the diagram. One of these admitted the thermometer; the other three, additional breaking devices. The thermometer was a mercury-in-glass instrument graduated in  $0.01^\circ$  from  $18$  to  $28^\circ$ . It was standardized at the Bureau of Standards. The gold-plated calorimeter can had a capacity of 1300 ml. The heating element in the heater-stirrer was made of constantan wire. It was wound on mica and housed in the thin copper vanes of the stirrer. The whole stirrer was carefully gold plated and then coated with a waterproof lacquer. The heating element was connected to the potentiometer and to an 8-volt, 320 ampere-hour lead storage battery by means of concentric mercury wells in the hard rubber disk, D.

The solute was introduced by means of small glass bulbs of 7-ml. capacity. These bulbs were closed either by fusion or by means of universal wax according to the nature of the contents. If wax was used the bulbs were always tested for leakage before using. The contents of the bulbs were introduced into the solvent by shattering the bulbs with the rod in the breaking device. The use of four small bulbs rather than one large one made possible a more gradual temperature change and, consequently, more accurate adiabatic control.

<sup>3</sup> Cohen, Moesveld and Helderman, *Z. physik. Chem.*, **112**, 141 (1924).

<sup>4</sup> Daniels, *THIS JOURNAL*, **38**, 1473 (1916).

The surrounding bath was heated by means of a 110-volt alternating current passing through the dilute copper sulfate solution. This gave uniform heating and avoided time lag. The bath was cooled by passing water through a copper cooling coil. E was a bypass. The surface of the bath was covered with a one centimeter layer of paraffin wax.

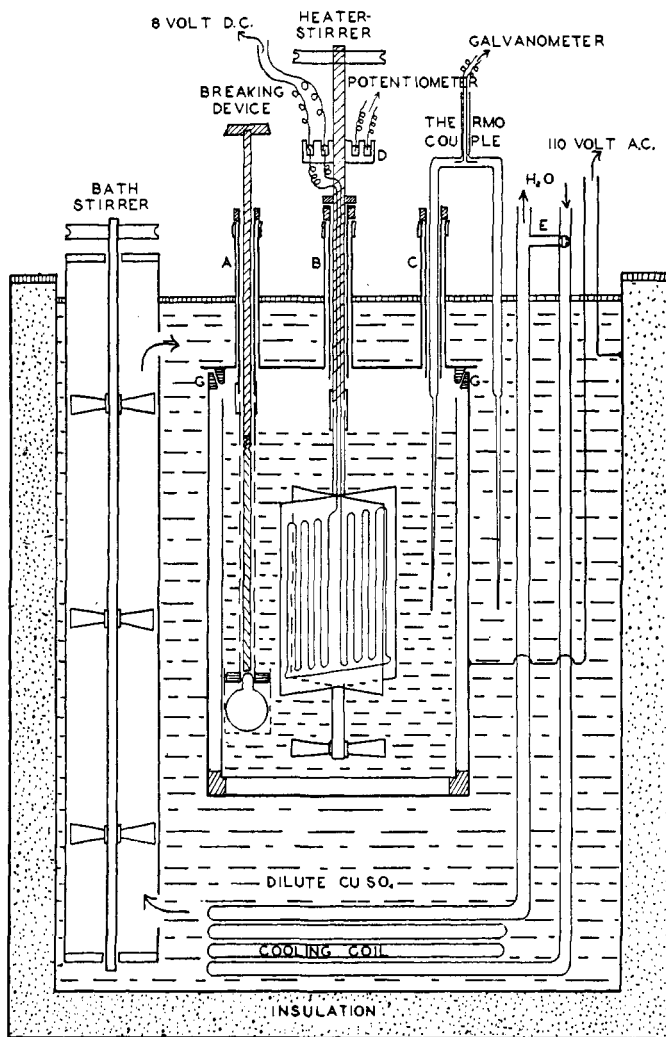


Fig. 1.

Adiabatic conditions were maintained between the calorimeter and the bath by the automatic control pictured at the right side of Fig. 2. The current from the photoelectric cell was amplified by means of a vacuum tube before passing through the sensitive relay. This arrangement kept the temperature difference between the bath and the calorimeter within  $0.01^\circ$ , even when the temperature was changing rapidly because of heat of reaction. Control tests showed that this was sufficiently accurate for this

calorimeter. The electrical power input into the calorimeter was measured by means of the hook-up diagrammed at the left of Fig. 2. The time of heating was measured to one-fifth of a second by means of an accurate stop watch. The magnitude of the current was determined by measuring the potential drop across the standard resistance. The energy data were calculated from the current and the resistance of the heater, assuming that the latter remained constant.

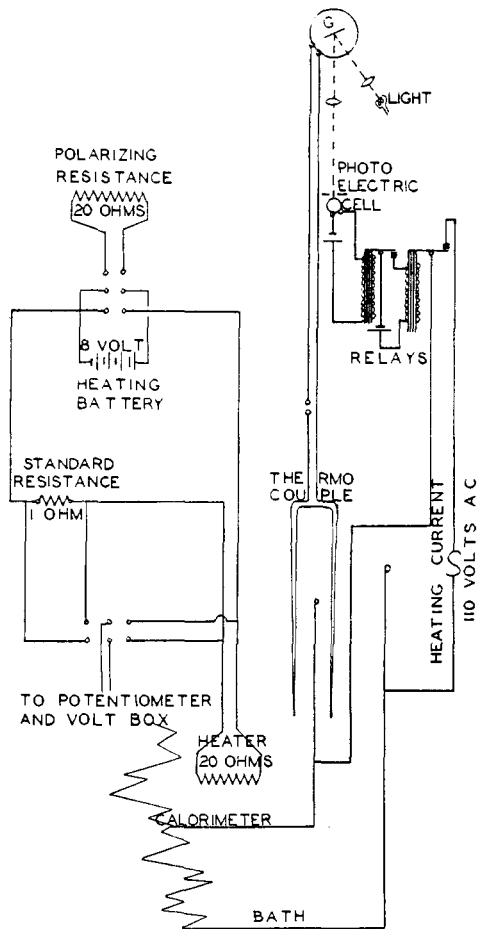


Fig. 2.

### Preparation of Materials

The calcium nitrate and the strontium nitrate were purified by recrystallizing the c. p. salts in the form of tetrahydrates, the calcium nitrate three times and the strontium nitrate twice. The temperature-composition and the temperature-vapor pressure diagrams for these hydrates enable one to choose the correct conditions for preparing the various hydrates. Similar data on strontium nitrate are being accumulated in this Laboratory. Calcium nitrate tetrahydrate was crystallized from solution at room temperature and dried over 60% sulfuric acid. Calcium nitrate trihydrate was prepared by melting together the stoichiometric ratios of the tetrahydrate and the anhydride. The crystallization of this melt at a constant temperature,  $51.1^\circ$ , gave assurance that the crystals formed were trihydrate. They were stored in a desiccator with tetrahydrate to constant weight. Calcium nitrate dihydrate was crystallized by evaporating a solution very slowly at  $51^\circ$  in a constant temperature bath. The large crystals formed were dried on filter paper and finally stored in a desiccator over the anhydride. Calcium ni-

trate anhydride crystals were dried to constant weight over phosphorus pentoxide.

Strontium nitrate tetrahydrate crystals were crystallized from solution at room temperature, which is a few degrees below the transition temperature. The drying of this salt gave considerable trouble. The tetrahydrate-anhydride mixture has a high vapor pressure; consequently, the tetrahydrate effloresces in air at ordinary humidities. The traces of anhydride formed tend to go into saturated solution of anhydride rather than back to tetrahydrate on taking up moisture. The difficulty was finally overcome by filtering and drying the crystals with filter paper in a constant humidity chamber at the vapor pressure of the saturated solution. These crystals when stored in a desiccator over a mixture of anhydride-tetrahydrate proved to be satisfactory. Strontium

nitrate anhydride was prepared by drying over phosphorus pentoxide. In all cases the crystals were analyzed for water content.

### Results

The data are given in Table I. Column 2 shows the weight of solute which was contained in the four small glass bulbs for each experiment.

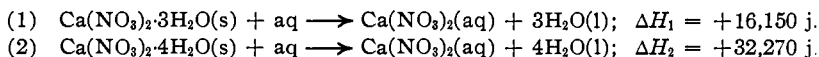
TABLE I  
HEATS OF SOLUTION OF THE SALTS IN 1000 GRAMS OF WATER

1 Salt	2 Wt. of salt	3 Final concn., moles anhyd. per 1000 g. H <sub>2</sub> O	4 $\Delta H$ joules/mole	5 Deviation from mean, %
Ca(NO <sub>3</sub> ) <sub>2</sub>	17.1846	0.1047	-18,450	+0.5
	20.2548	.1234	-18,620	+1.5
	20.2359	.1233	-18,200	-0.8
	20.3075	.1238	-18,380	+0.2
	14.8316	.0902	-18,740	+2.2
	15.0102	.0914	-19,300	+5.5
	16.3508	.0997	-17,830	-2.9
	16.0554	.0978	-17,880	-2.6
	16.7814	.1023	-17,770	-3.2
			Average, -18,350	
		I. C. T., -16,500		
Ca(NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	25.6322	0.1276	+12,750	+0.7
	25.6432	.1277	+12,580	-0.7
	25.5576	.1273	+12,670	0.0
			Average, +12,670	
		I. C. T., + 8,600		
Ca(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	20.1590	0.0919	+16,280	-4.5
	20.0377	.0914	+16,950	-0.6
	20.1371	.0918	+17,910	+5.1
			Average, +17,050	
		I. C. T., +22,000		
Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	20.3652	0.0857	+33,090	-0.2
	20.3519	.0856	+33,150	-0.1
	20.3525	.0856	+33,410	+0.7
	19.5599	.0823	+33,190	+0.1
	20.1012	.0846	+32,910	-0.8
	20.4306	.0860	+33,260	+0.3
		Average, +33,170		
		I. C. T., +30,300		
Sr(NO <sub>3</sub> ) <sub>2</sub>	30.6130	0.1446	+17,980	-0.4
	30.7677	.1453	+18,260	+1.2
	31.2931	.1478	+17,890	-0.8
		Average, +18,040		
		I. C. T., +18,900		
Sr(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	24.9957	0.0881	-52,490	+1.0
	23.9139	.0843	-51,410	-1.0
		Average, -51,950		
		I. C. T., -51,500		

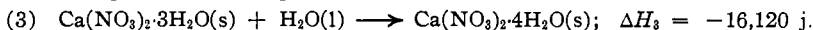
When these weights of salt were dissolved in the 1000 g. of water in the calorimeter, the concentrations in column 3 were obtained. These are expressed in moles of anhydride per 1000 g. of water. These concentrations vary from 0.08 to 0.13 molal. The changes in heat content,  $\Delta H$ , per mole of solute are tabulated in column 4.

Lange and Streeck<sup>5</sup> find for the heats of dilution of calcium nitrate and of strontium nitrate solutions from 0.1 *m* to infinite dilution  $\Delta H = -900$  joules and  $\Delta H = -500$  joules, respectively. These values added to the average heats of solution in Table I give the integral heats of solution when the salts are dissolved in an infinite quantity of water. These integral heats of solution are presented in Table II.

Experimental heats of hydration with liquid water, Table III, column 2, are obtained from these heats of solution. The method of summation may be illustrated by taking the trihydrate-tetrahydrate reaction as an example



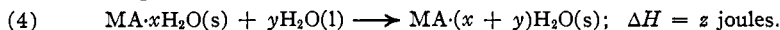
Subtracting (2) from (1) gives



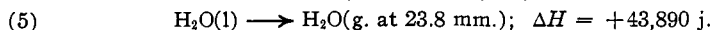
Here the symbol (aq) refers to infinite dilution, and  $\Delta H_3$  is the change in heat content for the hydration process.

#### Calculation of Heats of Hydration from Vapor Pressure Data.—

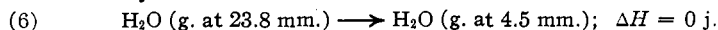
Equation (3) is a specific example of the equilibrium involved in the process of hydration. This equilibrium can be expressed by the general form of a chemical equation



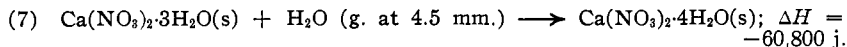
This heat of hydration can be calculated by resolving the reaction into a three-stage process. *Step 1* consists of the isothermal evaporation of *y* moles of water to form water vapor at its vapor pressure at, for example, 25°.



*Step 2* consists of the process of expansion of *y* moles of water vapor, at the vapor pressure of water, to the pressure that exists in equilibrium with the mixture of crystals.



since  $\Delta H = 0$  for the isothermal expansion of a perfect gas. *Step 3* consists of the reaction of the anhydride or the lower hydrate with *y* moles of water vapor to form the higher hydrate



If it is assumed that the partial molal volume of the *y* moles of water of hydration in the crystals is negligible compared to its volume in the vapor state and that the vapor behaves as a perfect gas at the low vapor pressures

<sup>5</sup> Lange and Streeck, *Z. physik. Chem.*, **157A**, 1 (1931).

TABLE II  
INTEGRAL HEATS OF SOLUTION

$\text{Ca}(\text{NO}_3)_2(\text{s})$	$+ \text{aq} \longrightarrow$	$\text{Ca}(\text{NO}_3)_2(\text{aq})$	; $\Delta H = -19,250 \text{ j.}$
$\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}(\text{s})$	$+ \text{aq} \longrightarrow$	$\text{Ca}(\text{NO}_3)_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l});$	$\Delta H = +11,770 \text{ j.}$
$\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}(\text{s})$	$+ \text{aq} \longrightarrow$	$\text{Ca}(\text{NO}_3)_2(\text{aq}) + 3\text{H}_2\text{O}(\text{l});$	$\Delta H = +16,150 \text{ j.}$
$\alpha\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}(\text{s})$	$+ \text{aq} \longrightarrow$	$\text{Ca}(\text{NO}_3)_2(\text{aq}) + 4\text{H}_2\text{O}(\text{l});$	$\Delta H = +32,270 \text{ j.}$
$\text{Sr}(\text{NO}_3)_2(\text{s})$	$+ \text{aq} \longrightarrow$	$\text{Sr}(\text{NO}_3)_2(\text{aq})$	; $\Delta H = +17,540 \text{ j.}$
$\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}(\text{s})$	$+ \text{aq} \longrightarrow$	$\text{Sr}(\text{NO}_3)_2(\text{aq}) + 4\text{H}_2\text{O}(\text{l});$	$\Delta H = +51,450 \text{ j.}$

TABLE III  
CHANGES IN HEAT CONTENT, AND IN FREE ENERGY, IN JOULES AT 25°

Reaction		$\Delta H$		$-\Delta F$ Calculated
		Experimental	Calculated	
$\text{Ca}(\text{NO}_3)_2(\text{s})$	$+ 2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}(\text{s})$	-31,000	-30,800	11,780
$\text{Ca}(\text{NO}_3)_2(\text{s})$	$+ 4\text{H}_2\text{O}(\text{l}) \longrightarrow \text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}(\text{s})$	-51,500	-59,700	20,480
$\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}(\text{s})$	$+ \text{H}_2\text{O}(\text{l}) \longrightarrow \text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}(\text{s})$	- 4,400	-11,500	5,130
$\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}(\text{s})$	$+ 2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}(\text{s})$	-20,500	-17,200	8,820
$\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}(\text{s})$	$+ \text{H}_2\text{O}(\text{l}) \longrightarrow \text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}(\text{s})$	-16,100	-16,900	4,130

of the hydrates, the Clapeyron-Clausius equation can be applied to such systems in the form

$$(8) \quad \frac{d \ln p}{d(1/T)} = -\frac{\Delta H}{R}$$

where  $-\Delta H$  is the heat of hydration when the anhydride or a lower hydrate unites with water vapor to form a higher hydrate. This permits us to calculate  $\Delta H$  for equation (7). The sum of these three steps gives the heat of hydration with liquid water represented in reaction 3 above. These values, calculated from vapor pressure data, are tabulated in Table III, column 3, for comparison with the experimental heats.

**Accuracy of Results.**—The sources of error in calculated and observed heats of solution must be considered. Individual determinations of the heat capacity of the calorimeter were consistent to within 28 joules in a total of 4500 joules. This corresponds to a temperature error of less than  $0.004^\circ$ , the limit of reliability of a mercury-in-glass thermometer graduated in  $0.01^\circ$ .<sup>6</sup>

A mathematical analysis of the data in Table I indicates that the error in measurement of heats of solution varies from 0.3 to 3%. The errors in measuring the heats of solution are considerably larger than the error in determining the heat capacity of the calorimeter. These are caused in large part by difficulty in preparing the hydrates in a pure state. This was particularly true of  $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  since they had to be prepared from concentrated, viscous solutions at high temperatures.

Errors in calculating heats of hydration from vapor pressures are: (1) Errors due to vapor pressure measurements. These amount to  $\approx 900$  joules, corresponding to an error of  $\approx 0.05$  mm. (2) Uncertainty of at least 0.1% in latent heats of vaporization. This corresponds to from 50 to 200 joules. (3) Errors in the Clapeyron-Clausius equation introduced by assuming water vapor to be a perfect gas. This amounts to from 190 joules to 760 joules. Thus the maximum deviation in the calculated heats of hydration is 4560 joules or, at most, 13.3%.

It is interesting to compare observed values of vapor pressure with those calculated from heats of hydration. Taking  $T$  as  $25^\circ$  and  $\Delta(1/T)$  as 0.0001, we find at  $35^\circ$

Equilibrium.....	Tetra-tri.	Tetra-di.	Tetra-anhyd.	Tri-di.	Di-anhyd.
Calcd. vapor pressure, mm.....	9.9	8.1	6.3	5.1	4.8
Obs. vapor pressure, mm.....	10.0	8.0	6.5	5.5	4.9

In general, the concordance is very satisfactory.

**Free Energy of Hydration.**—An expression for the free energy change,  $\Delta F$ , for the hydration process can be derived by letting the process take place in the three steps already mentioned. For steps 1 and 3

$$(9) \quad -\Delta F = 0$$

<sup>6</sup> Bureau of Standards Circular No. 8.

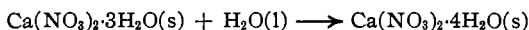


Step 2 consists of the isothermal expansion of water vapor. If water vapor behaves as a perfect gas,  $\Delta p v = 0$ , and

$$(10) \quad -\Delta A = -\Delta F = nRT \ln (p_w/p_s)$$

The sum of these three steps leaves equation (10) as the decrease in free energy of the hydration process. The decrease in free energy is tabulated in Table III, column 4.

**Change in Heat of Hydration and Change in Free Energy with Change in Temperature.**—Since  $\ln p$  plotted against  $1/T$  gives a straight line, step 3 in the hydration process, that is, the heat of hydration with water vapor, remains constant at various temperatures. The change in heat of hydration with liquid water with change in temperature, then, is due to changes in the latent heat of vaporization of water with change in temperature. Heats of hydration and latent heats are tabulated in Table IV for the system



Values for the decrease in free energy,  $-\Delta F$ , for the same process, calculated by means of equation (10) at various temperatures, are tabulated in the same table.

TABLE IV

Temp.....	$\Delta H$ AND $-\Delta F$ AT VARIOUS TEMPERATURES				
	20°C.	25°C.	30°C.	35°C.	40°C.
Step 1.	+44,102 j.	+43,886 j.	+43,688 j.	+43,481 j.	+43,273 j.
Step 3	-60,800	-60,800	-60,800	-60,800	-60,800
$\Delta H$	-16,698	-16,914	-17,112	-17,319	-17,527
$p_w/p_s$	17.5/3.0	23.8/4.5	31.8/6.8	42.2/10.0	55.3/14.8
$-\Delta F$	+4299	+4129	+3888	+3689	+3432

This table shows that there is a small increase in heat of hydration and a small decrease in the decrease in free energy with increasing temperatures for this reaction.

### Summary

Integral heats of solution of the hydrates and the anhydride of calcium nitrate and of strontium nitrate have been measured.

Heats of hydration have been calculated from these heats of solution. The same heats of hydration have been calculated from the latent heat of vaporization of water and the vapor pressure-temperature measurements above both the stable and the metastable eutectic mixtures of crystals.

The change in free energy of hydration has been calculated.

The changes in heat content and in free energies of hydration with change in temperature have been calculated.