ally (*7*) are somewhat higher than this, but based upon the assumptions used, the thermodynamic consistency is better at the lower values.

The theoretical calculations clearly indicate the very large effect that even small differences in vapor pressure have in attaining thermodynamic consistency of data. This shows that future experiments should devote considerable effort toward minimizing errors in vapor pressure data for sodium and other alkali metals.

The present study has shown rather definitely that sodium vapor acts very much as other vapors with regard to supersaturation. It also has shown, at least for the convergent section of this small nozzle, that chemical equilibrium between species is not attained. Again, it should be remembered that all of these results would be negated should it be proved that sodium does not act as a perfect gas near the saturated vapor conditions.

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Changes in Enthalpy During the Heating of $CaHPO_4 \cdot 2H_2O$

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The changes in enthalpy which occur when $CaHPO_4 \cdot 2H_2O$ is heated up to 1300° C. have been determined in a humid atmosphere by the DTA method. The heats were determined for the following reactions: dehydration of $CaHPO_4 \cdot 2H_2O$ to give two moles of water vapor at 135° C., 21.1 kcal./mole; intermolecular dehydration of $CaHPO_4$ to give γ-$Ca_2P_2O_7$ at 430° C., 7.2 kcal./mole; transitions form γ to β at 850° C., 0.20 kcal./mole, and β to α-$Ca_2P_2O_7$ at 1220° C., 0.76 kcal./mole respectively. (All heats are based on one mole of $CaHPO_4 \cdot 2H_2O$.) The stability of γ $-Ca_2P_2O_7$ is discussed on the basis of these data.

THE DEHYDRATION of $CaHPO_4 \cdot 2H_2O$ has been studied by Vol'fkovich and Urusov (*12*), Boullé and du Pont (*3*) and Rabatin, *et al.*, (*10*) since 1950. All of these authors concur on the importance of the humidity above the sample on the rate of the dehydration process which occurs. In humid air, the reaction proceeds more rapidly than in dry air or vacuum, and only crystalline products are formed. In 1960, Rabatin, *et al.*, (*10*) demonstrated by differential thermal analysis (DTA), thermogravimetric analysis (TGA), and x-ray diffraction techniques that in humid air single peaks occurred for the transition of $CaHPO_4 \cdot 2H_2O$ to the anhydrous salt and from the anhydrous salt to $Ca_2P_2O_7$. In dry air, they obtained several additional peaks which were attributed to amorphous phases and $CaHPO_4$ with unknown hydrate content. The behavior above 600° C. was not previously reported.

These observations by DTA in both humid air and dry air have been confirmed. Because the complex behavior in dry air or vacuum does not lend itself to straightforward interpretation, humid atmosphere was used for measurement of the heats of reactions which occur when $CaHPO_4 \cdot 2H_2O$ is heated to 1300° C. The heats were determined by the DTA method using the internal standard technique described by Barshad (*2*); however, the additional refinement of including heat capacities of the solids has been made.

EXPERIMENTAL

Materials. The $CaHPO_4 \cdot 2H_2O$ used as the starting material for the DTA curves had a surface area of 0.7 $m.^2/gm.$ and was prepared by the method of Aia, *et al.*, (*1*). An ammoniacal solution of $CaCl_2$ was added to a solution of $NH_4H_2PO_4$ at room temperature. The precipitate was washed with dilute phosphoric acid solution and then with acetone before allowing to dry. The γ-$Ca_2P_2O_7$ was prepared by heating $CaHPO_4 \cdot 2H_2O$ at 400° C. for 48 hours.

The $CaCO_3$ used was reagent grade material produced by Baker and Adamson and dried at 110° C. The DTA reference material was γ-alumina prepared for high temperature combustions by Fisher Scientific Company.

Apparatus and Procedure. A Robert L. Stone differential thermal analysis apparatus model DTA-12AC was used in this study. The furnace, Model DS 2 and the palladium cell have a heating range up to 1400° C. The humid atmosphere was provided by allowing about 10 grams of distilled water to be absorbed into the porous brick at the base of the cell before starting the programmed temperature rise. Heating rates of 4 and 10° C. per minute were used.

A blended mixture of $CaHPO_4 \cdot 2H_2O$ and $CaCO_3$ was placed in the sample well and γ-alumina in the reference well for measurement of the heats of dehydration of $CaHPO_4 \cdot 2H_2O$ and the intermolecular dehydration of $CaHPO_4$ to form γ-$Ca_2P_2O_7$. The heat of transition to the β-$Ca_2P_2O_7$ was determined on a sample of $CaHPO_4 \cdot 2H_2O$ in which the $CaCO_3$ was omitted because of the $CaCO_3$ decomposition at about 815° C. masks this transition. No correction was made for the occurrence of the γ to β-$Ca_2P_2O_7$ transition when $CaCO_3$ was used because the error involved was less than 0.3%. The peak areas were determined by weighing traces of the thermogram on uniform density paper.

RESULTS AND DISCUSSION

Figure 1 shows the DTA patterns produced when $CaHPO_4 \cdot 2H_2O$ and γ-$Ca_2P_2O_7$ were used as the starting materials. The identification of the products of the reactions was made by x-ray diffraction. The following sequence of reactions occurs.

$$CaHPO_4 \cdot 2H_2O \rightarrow CaHPO_4 + 2H_2O(g) \quad (1)$$

$$CaHPO_4 \rightarrow \tfrac{1}{2}\, Ca_2P_2O_7\,(\gamma) + \tfrac{1}{2}\, H_2O(g) \quad (2)$$

$$\tfrac{1}{2}\, Ca_2P_2O_7\,(\gamma) \rightarrow \tfrac{1}{2}\, Ca_2P_2O_7(\beta) \quad (3)$$

$$\tfrac{1}{2}\, Ca_2P_2O_7\,(\beta) \rightarrow \tfrac{1}{2}\, Ca_2P_2O_7(\gamma) \quad (4)$$

The enthalpy changes for these reactions were determined using $CaCO_3$ as the internal standard. The heat of decomposition (*11*) of $CaCO_3$, 42.9 kcal./mole at 25° C., was corrected to the decomposition temperature of 815° C. when the DTA experiments were carried out at atmospheric pressure and a heating rate of 4° C. per minute. The temperature correction was made using the following equation:

$$\Delta H_T = \Delta H_{298^\circ\,K.} + \int_{298^\circ\,K.}^{T} \Delta C_p\, dT.$$

The heat capacities (*7*) compiled by K.K. Kelley were used. The heat of decomposition at 815° C. was calculated to be 40.2 kcal./mole.

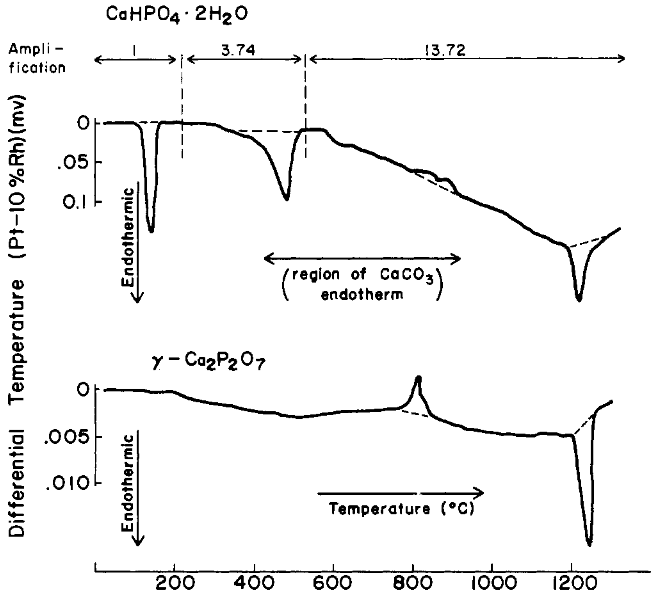

Figure 1. DTA thermograms for $CaHPO_4 \cdot 2H_2O$ and γ-$Ca_2P_2O_7$ up to 1300° C. at 10°/min. in a humid atmosphere

Table I. Enthalpy Changes by DTA Method (Kcal./Mole)

Reaction	Heating Rate °/min.	T(° C.)	ΔH_T
1	4	135	21.3, 20.9
2	4	430	6.9, 7.5
3	10	850	−0.17,−0.23
4	10	1220	0.85, 0.68

The enthalpy changes in duplicate for the reactions are listed in the Table I.

The enthalpy of dehydration of $CaHPO_4 \cdot 2H_2O$ is calculated by subtracting the heat of vaporization (18.6 kcal.) of two moles of water at 135° C. (*9*) from the heat of reaction (*1*). This gives 2.5 ± .2 kcal./mole which is compared with a value of 4.4 kcal./mole at 25° C. from heats of solution measurements (*6*). No previous measurements have been reported on the intermolecular dehydration of $CaHPO_4$ or the conversion of γ-$Ca_2P_2O_7$. However, a value of 0.81 kcal./mole has been determined for the β to α transition at 1140° C. from heat capacity data (*5*) This agrees within the experimental error with our value of 0.76 ± 0.08 kcal./mole at 1220° C.

The heat of formation of α, β or γ-$Ca_2P_2O_7$ at 25° C. is estimated to be 798.6 ± 2 kcal./mole based upon the following data: heat capacities of $CaSO_4$ (*8*), which is isoelectronic with $CaHPO_4$, water (*7*) and β-$Ca_2P_2O_7$ (*5*); the known heats of formation (*11*) of $CaHPO_4$ and H_2O at 25° C.; and the heat of reaction (*2*) at 430° C.

The transition from γ to β-$Ca_2P_2O_7$ is exothermic while all the other reactions are endothermic. This is observed when the starting material is $CaHPO_4 \cdot 2H_2O$ or the γ-$Ca_2P_2O_7$ prepared as described in the previous section. Buerger (*4*) argues correctly that a transition which occurs between stable phases upon increasing temperature cannot be exothermic because of the third law of thermodynamics. We propose that γ-$Ca_2P_2O_7$ is a metastable phase which forms upon dehydration of $CaHPO_4$. Previous work in this laboratory on the interpretation of the x-ray diffraction patterns of γ and β-$Ca_2P_2O_7$ supports this hypothesis in that there are few unique peaks associated with the γ phase not present with the β phase, and the β-peaks are sharper and more well defined.

Also, the two phases were reported to be indistinguishable by heat capacity measurements (*5*). However, very precise work is required to determine the heat of the γ to β transition because we have shown it to be very small.

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Heat and Free Energy of Formation of the *Cis*- and *Trans*-Decalins, Naphthalene and Tetralin from 298° to 1000° K.

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Values of the heat (ΔH_f°) and free energy(ΔF_f°) and log$_{10}$ of the equilibrium constant of formation (K_f) are calculated for the *cis*- and *trans*-decalins, naphthalene, and tetralin in the ideal gas state from 298° to 1000° K. from thermodynamic data.

VALUES for the free energy of formation of tetralin in the gaseous state are calculated by combining published thermodynamic data on napthalene and published measurements of the equilibrium in the hydrogenation of naphthalene to tetralin. Because no values for the free energy of formation of either naphthalene or decalin were found in the literature, they are also included in Table I.

The heat and free energy of formation of the *cis*- and *trans*-decalins from 298.16° to 1000° K. were calculated from the heat content and free energy functions of hydrogen (*8*), carbon (*8*), and the *cis*- and *trans*-decalins (*7*), and the measured heats of formation of the *cis*- and *trans*-decalins (*9*) at 298.16° K.

The heat and free energy of formation of naphthalene were calculated similarly from the heat content and free energy functions of naphthalene (*4*) and the measured heat of formation of naphthalene (*9*) at 298.16° K. The heat and free energy values at 298.16° K. agree with those published recently by Miller (*6*); however, the values for the free energy of formation at higher temperatures in the latter paper are in error. (In a private letter Miller's corrected values at 400 and 500° K. agree with those in Table I.).

The thermodynamic data for tetralin in the ideal gas state for the temperature range 298° to 1000° K. were obtained as follows:

1. Values of the heat capacity of the liquid in the temperature range 320° to 480° K. were obtained by extrapolation of the heat capacity data in the 250 to 320° K. range given by McCullough, *et al.*, (*5*). The entropy values of the liquid were obtained by integration of the equation (least squares fit) representing the heat capacity as a function of temperature.
2. Values of the entropy of vaporization at several temperatures were calculated from vapor pressure data given by Mair and Streiff (*3*). The following Antoine equation was found to represent their three measurements of the vapor pressure.

$$\log_{10} P_{\text{mm}} = 6.98280 - \frac{1667.693}{198.987 + t^\circ \text{C.}}$$

It was assumed that the vapor volume follows the Berthelot equation of state with critical constants T_c = 719.2° K. and P_c = 34.67 atm. (*1*). The Berthelot equation was used, also, in the correction of the entropy to the ideal gas state.