THE HEATS OF FORMATION OF TRIMANGANOUS PHOSPHATE AND TRIMAGNESIUM PHOSPHATE

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The heats of formation of manganous and magnesium orthophosphates from their constituent oxides, have been determined by heat of solution calorimetry and the following results obtained :

3 MnO (c) + P₂O₅ (ortho) = Mn₃P₂O₈ (c); $\Delta H_{348^{\circ}\kappa} = -105,230 \pm 530$ cal, 3 MgO (c) + P₂O₅ (ortho) = Mg₃P₂O₈ (c); $\Delta H_{348^{\circ}\kappa} = -110,940 \pm 620$ cal. The heats of solution of trimanganous phosphate, trimagnesium phosphate, manganous oxide, magnesium oxide and phosphorus pentoxide in hydrochloric acid have been measured at 75° C and the results employed to calculate the heats of formation of the two phosphates from their constituent oxides.

EXPERIMENTAL

The methods and equipment employed were those described previously ¹ except that samples were introduced into the calorimeter in sealed glass ampoules A (see fig. 1). These were mounted on a glass rod freely movable inside a glass tube B which passed through one of the apertures in the calorimeter lid. The ampoule and its holder were placed in position when the calorimeter was assembled. The sample

was introduced into the acid by breaking the ampoule on the striker C. Because the submerged ampoule was at the same temperature as the calorimeter liquid, the usual correction for differences in temperature between sample and liquid was not required. The solvent employed was 850 ml of 1 N HCl at 75° C.

MATERIALS.—*Manganous orthophosphate.*—This compound was prepared as described elsewhere : ² the product contained 59.7 % MnO and 40.0 % P_2O_5 (theoretical : 59.97 % MnO and 40.03 % P_2O_5).

Magnesium orthophosphate.—A stoichiometric mixture of magnesium oxide and diammonium hydrogen phosphate was heated in a platinum crucible to 1000° C. The product, i.e. $Mg_3P_2O_8$, was ground, mixed and reheated above its melting point, 1348° C, recrystallized by slow cooling and then quenched. Analysis gave 45.7 % MgO and 54.1 % P₂O₅ (theoretical : 46.01 % MgO and 53.99 % P₂O₅).

Manganous oxide.—Pure manganous oxide (99.8 %) was prepared by the method described by King.³

Magnesium oxide.—A.R. material was heated to constant weight at 1500° C in air. Ampoules were filled with this substance in a conventional "dry-box" and sealed immediately.

Phosphorus pentoxide.—According to Hill, Faust and Hendricks ⁴ phosphorus pentoxide has three allotropic forms, hexagonal, orthorhombic and tetragonal. Their method of preparing the orthorhombic form was adopted as follows.

Phosphorus pentoxide of a good reagent grade was first sublimed *in vacuo*, the glass receiver being sealed off without exposure of the contents to air, and then heated to $380-390^{\circ}$ C for 2 h to convert the hexagonal form to the orthorhombic modification. Refractive index measurements on the product agreed with the findings of the above mentioned authors. Glass ampoules were then filled using the "dry-box". The orthorhombic form of phosphorus pentoxide was used because it dissolved less violently in 1 N HCl at 75° C than did the hexagonal form.

RESULTS

In measuring the heats of solution of phosphorus pentoxide and phosphates, the concentration of the dissolved substance in each case was 0.019 mole/l. of solution. For the heat of solution determinations of manganous and magnesium oxides, the concentration in each case was 0.057 mole/l.

The following are the results obtained.

(a)
$$Mn_3P_2O_8(c) + 6 \text{ HCl } (sol) = 3 \text{ MnCl}_2(sol) + 2 \text{ H}_3PO_4(sol)$$

 $\Delta H_{348^\circ K} = -28,840, -28,730, -28,970, -28,960, -29,030,$
 $mean = -28,910 \pm 120 \text{ cal.}$
(b) $Mg_3P_2O_8(c) + 6 \text{ HCl } (sol) = 3 \text{ MgCl}_2(sol) + 2 \text{ H}_3PO_4(sol)$

$$\Delta H_{348^{\circ}\kappa} = -47,790, -47,580, -47,660, -47,830, -47,670, -47,610,$$

mean = $-47,690 \pm 100$ cal.

(c) 3 MnO (c) + 6 HCl (sol) = 3 MnCl₂ (sol) + 3 H₂O (l)

 $\Delta H_{348^{\circ}\mathbf{k}} = -81,540, -82,380, -82,170, -81,570, -81,720, -81,990,$ mean = -81,890 ± 335 cal.



8

HEATS OF FORMATION

(d)
$$3MgO(c) + 6 HCl(sol) = 3 MgCl_2(sol) + 3 H_2O(l)$$

 $\Delta H_{348^{\circ}K} = -106,620, -106,230, -105,870, -106,920, -105,900, -106,740,$
mean = -106,380 ± 450 cal.
(e) $P_2O_5(o) + 3 H_2O(l) = 2 H_3PO_4(sol)$
 $\Delta H_{348^{\circ}K} = -51,720, -52,100, -52,140, -52,600, -52,320, -51,910, -52,950$

 $mean = -52,250 \pm 420 \text{ cal.}$

The symbols used above have the following significance :---

(o) orthorhombic, (c) crystalline, (sol) in solution.

It should be noted that the solution of phosphorus pentoxide was carried out in hydrochloric acid containing dissolved manganous chloride (first three results) or magnesium chloride (last four results), at concentrations of 0.057 M. There was no significant difference between the two sets of results. This implies that the difference between the heat of solution of P_2O_5 in HCl containing MnCl₂ and in HCl containing MgCl₂ is not detectable by the method employed and the use of the grand mean is justified.

HEATS OF FORMATION OF MANGANOUS ORTHOPHOSPHATE AND MAGNESIUM ORTHO-PHOSPHATE.—Combination of the results given in (a), (c) and (e) above leads to the equation:

$$3 \operatorname{MnO} (c) + P_2O_5 (o) = \operatorname{Mn_3P_2O_8} (c); \ \Delta H_{348^\circ \kappa} = -105,230 \pm 550 \text{ cal},$$
(1)

and of results in (b), (d) and (e) to

3 MgO (c) + P₂O₅ (o) = Mg₃P₂O₈ (c);
$$\Delta H_{348^{\circ}K} = -110,940 \pm 620$$
 cal. (2)

DISCUSSION

In order to compare the results given above with those determined previously, it is convenient to convert them to heats of formation from elements in their standard states.

The heats of formation of manganous oxide, magnesium oxide and phosphorus pentoxide, from their elements in their standard states, have already been determined; these values are given in the following table:

Mn (c) $+\frac{1}{2}$ O₂ (g) = MnO (c); $\Delta H^{\circ}_{298^{\circ}K} = -92,040 \pm 110 \text{ cal},5$ (3)

Mg (c) + $\frac{1}{2}$ O₂ (g) = MgO (c); $\Delta H^{\circ}_{298^{\circ}K} = -143,840 \pm 50 \text{ cal},6$ (4)

 $2P(white) + 2\frac{1}{2}O_2(g) = P_2O_5(o); \quad \Delta H^{\circ}_{298^{\circ}\kappa} = -368,400 \pm 7,000 \text{ cal.}^{7-12}$ (5)

The data on the heat of formation of phosphorus pentoxide are not concordant; the above value is the mean with an uncertainty of approximately \pm 7 kcal.

Combination of eqn. (1), (3) and (5) gives

3 Mn (c) + 2 P (white) + 4 O₂ (g) = Mn₃P₂O₈(c);

$$\Delta H_{298^{\circ}\kappa}^{\circ} = -749,750 \pm 7,000 \text{ cal}, (6)$$

and the summation of eqn. (2), (4) and (5) gives

3 Mg (c) + 2 P (white) + 4 O₂ (g) = Mg₃P₂O₈ (c);

$$\Delta H_{298^{\circ}\kappa}^{\circ} = -910,860 \pm 7,000 \text{ cal.} (7)$$

It should be noted that the reactions (1) and (2) are assumed to have taken place at 298° instead of 348° K, because appropriate calculations could not be done in the absence of specific heat against temperature data on these phosphates. Nevertheless, the error involved in such an assumption is negligible compared with the magnitude of the uncertainty in eqn. (5).

Berthelot ¹³ determined the heats of solution of the two phosphates and recorded heats of formation from elements in their standard state as follows:

$$\Delta H_{298^{\circ}\kappa}^{\circ}$$
 (Mn₃P₂O₈) = -737,500 cal, and $\Delta H_{298^{\circ}\kappa}^{\circ}$ (Mg₃P₂O₈) = -910,600 cal.

There is a good agreement between the authors' results and those of Berthelot, particularly with respect to the heat of formation of magnesium orthophosphate.

Rossini *et al.*¹⁴ appear to have recalculated Berthelot's results and give values of -771,000 and -961,500 cal, for the heats of formation of manganous orthophosphate and magnesium orthophosphate, respectively. It is not clear how the recalculation has been carried out; attention should be called to what appears to be a misprint—manganous orthophosphate is listed as $Mn_2(PO_4)_3$.

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373