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# A Study of the Hydration of Calcium Orthoplumbate. VII. The Mechanism of the Formation of Hydrate

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The hydration processes of calcium orthoplumbate are studied by means of a twin-type conduction calorimeter. The curves of the differential electromotive force vs. the hydration time have two characteristic maxima, corresponding to two exothermic processes: the first one is due to the immersion and dissolution of calcium orthoplumbate, while the second one is caused by the formation of crystalline hydrates. The heat liberated by the first process is about 1.14 cal./g. $Ca_2PbO_4$, while that liberated by the second process is about 52.22 cal./g. $Ca_2PbO_4$. The reaction in the second process proceeds by the 2/3 order; this may be explained by assuming that the rate of the reaction is determined by the surface area of the calcium orthoplumbate being hydrated.

Many investigations of the reactions of calcium orthoplumbate with water have been reported[1] but most of the investigations have been those of reactions above 100°C; few experiments[2] have been carried out concerning hydration below 100°C.

In previous papers[2] we reported the compositions of completely hydrated products of calcium orthoplumbate and the process of hydrating them at various temperatures below 100°C; we made our study by the use of X-ray diffraction analysis, thermobalance analysis, chemical analysis, and electron microscopy. In this paper, the hydration of calcium orthoplumbate will be examined by a twin-type conduction microcalorimeter in order to obtain the heats of hydration and, therefrom, some information on the mechanism of the hydration process.

## Experimental

**Material.**—*Calcium Orthoplumbate.* — $Ca_2PbO_4$ (or $2CaO \cdot PbO_2$) was prepared by heating an equimolar mixture of lead oxide and calcium carbonate in air at 700°C for 8 hr. The product was identified by X-ray diffraction and chemical analysis. The composition found was $PbO_2$: 66.71%, CaO: 32.00%, and free calcium as $Ca(OH)_2$: 1.47%. The specific gravity was 5.7. The specific surface area determined by the BET method with an nitrogen adsorption of 3.01 $m^2/g$. Four chemical reagents, lead oxide, lead peroxide, calcium hydroxide, and calcium carbonate, were employed as reference samples for the analysis of X-ray diffraction patterns, using Cu$K_\alpha$ radiation.

## Apparatus and Procedure

**Apparatus for Hydration Reaction.**—*Calorimeter.*—The twin-type conduction calorimeter employed in this work was a commercial model, CM-502, of Ôyodenki Kenkyujo.[3] While this calorimeter is based on the principle which Tian & Calvet first developed, a brief description of the apparatus will be appropriate here. The apparatus is shown in Fig. 1. The main part of the apparatus consists of two pairs of similar calorimeters, each having a 70 ml. reaction cell, a stirrer,

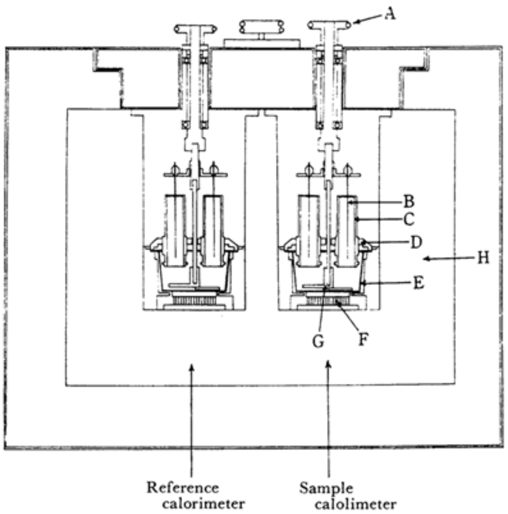

Fig. 1. Principal diagrams of twin-type conduction calorimeter.
A, Pulley; B, Needle; C, Sample-holding tube; D, Lid; E, Reaction cell; F, Thermoelement; G, Stirrer; H, Aluminum block (standard bed)

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[1] J. W. Mellor, "Comprehensive Treatise of Theoretical and Inorganic Chemistry," Vol. 7, Longmans, Green and Co., London (1931), Term of the Plumbate.

[2] M. Koishi and K. Meguro, *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zasshi)*, **67**, 2001, 2005 (1964); M. Koishi and K. Meguro, *J. Japan Soc. Colour Material (Shikizai Kyokaishi)*, **39**, 20 (1966).

[3] K. Hagiwara, *An Explanatory Note of the CM-502-type Conduction Calorimeter* (Ôyodenki Kenkyujo) (1963); K. Amaya, *Bussei*, **4**, 588 (1963) (in Japanese).

two sample-holding tubes, breakers, a calibrated electric heater, and a thermoelement. The two calorimeters are surrounded by an aluminum block. All the tubes are sealed with rubber membrane and are supported by a lid attached to a main rod from the top plate of the aluminum block. The needles for breaking the rubber film in order to drop the sample into water are connected to the stirrer. The needles slip down with the rotation of the stirrer and so break the rubber membrane. The temperature difference between the two calorimeters produced by the immersion of sample into water is detected by a thermoelement. The electromotive force of the thermoelement of this apparatus is 6.5 mV./deg., and the optimum sensitivity is about $5\times10^{-4}$°C under the present operating conditions.

**Procedure.**—After the bottom of all the tubes have been sealed with rubber membrane, about 1.0—14.0 g. of calcium orthoplumbate is weighed into one of the sample-holding tubes of the sample calorimeter. This tube and another empty one* of the sample calorimeter are set on a lid. Another pair of empty tubes are placed on a lid in the reference calorimeter to serve as compensators. Equal volumes of distilled water (20 ml.) are then introduced both into the sample cell and into the reference cell. After the two calorimeters have been set in position, they are kept for about 5 hr. at the desired temperature in order to attain an equilibrium. Then, the sample is dropped into water and the heat liberated in the calorimeter is recorded as the differential electromotive force. After the hydration reactions of calcium orthoplumbate have been completed in the calorimeter, a known amount of electrical energy is supplied to one of the calorimeters to calibrate for the heat liberated. One example of the recorded thermograms is shown in Fig. 2. The amount of heat ($Q_1$ cal.) liberated by the reaction is calculated by the following equation:

$$Q_1 = \frac{S_1}{S_2} \times Q_2$$

where $S_1$ denotes the area under the curve of the diagram, corresponding to the liberated heat $Q_1$, and where, similarly, $Q_2$ and $S_2$ denote the heat supplied as electrical energy and the corresponding area respectively.

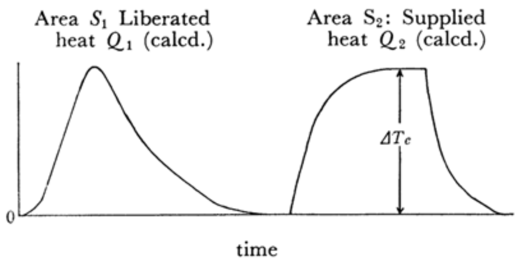
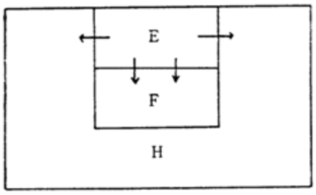


Fig 2. Standard diagram of record.

**The Determination of the Apparatus Constant of the Calorimeter.**—The calorimeter of this experiment is schematically shown by the block diagram in Fig. 3. The heat liberated in the reaction cell, E, is conducted away in two ways; one is the direct escape from E to H (aluminum block), and the other is that through F (the thermoelement). If the heat is assumed to escape exclusively through the thermoelement, F, both the generation and the absorption of the heats by the sample per unit time ($dQ/dt$) are given by the following equation:



E : Reaction cell
F : Thermoelement
H : Aluminum block

Fig. 3. Block diagram of calorimeter.

$$dQ/dt = \sigma\cdot\Delta T + H\cdot d(\Delta T)/dt \qquad (1)$$

where $Q$ denotes the heat liberated in the sample calorimeter, $\sigma$ is the effective thermal transmissive coefficient of the thermoelement, F (cal./deg. sec.), and $\Delta T$ is the temperature difference between the reaction cell and the cell of the reference calorimeter. The constant $H$ stands for the effective heat capacity of E.

The $\Delta T$ recording for the electrical energy in Fig. 2 tends to level off, and in this region Eq. 1 reduces to:

$$\sigma = W/\Delta T_e \qquad (2)$$

where $W$ denotes the supplied electrical energy (watt), and $\Delta T_e$ is the temperature difference from the base line at the stationary state, because $d(\Delta T)/dt=0$ at the stationary state. $H$ is calculated by:

$$d\ln(\Delta T) = -\frac{\sigma}{H}dt \qquad (3)$$

from the $\Delta T$ recording curve after the supply of electrical energy is stopped.

The values of $\sigma$ and $H$ obtained here are $4.72\times10^{-2}$ cal./deg. sec. and 25.30 cal./deg. Using these values, Eq. 1 may be rewritten as:

$$dQ/dt = 4.72\times10^{-2}\times\Delta T+25.30\times d(\Delta T)/dt \qquad (4)$$

## Results and Discussion

**The Heat of the Hydration of Anhydrous Calcium Orthoplumbate.**—The determination of

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* The empty tube is for use in the case of a bulky sample.

Table I. The values of the heat liberated during the hydration

| $Ca_2PbO_4/H_2O$ (molar ratio) | Duration of experiment, hr | Total heat liberated, cal. | Heat liberated, cal./g. | | |
|---|---|---|---|---|---|
| | | | First process | Second process | Total |
| 1/30 | 18 | 636.28 | 1.47 | 53.10 | 54.57 |
| 1/70 | 18 | 268.50 | 1.20 | 52.50 | 53.70 |
| 1/200 | 18 | 90.70 | 1.03 | 50.80 | 51.83 |
| 1/300 | 18 | 62.06 | 1.13 | 52.10 | 53.23 |
| 1/400 | 18 | 46.80 | 0.88 | 52.61 | 53.49 |

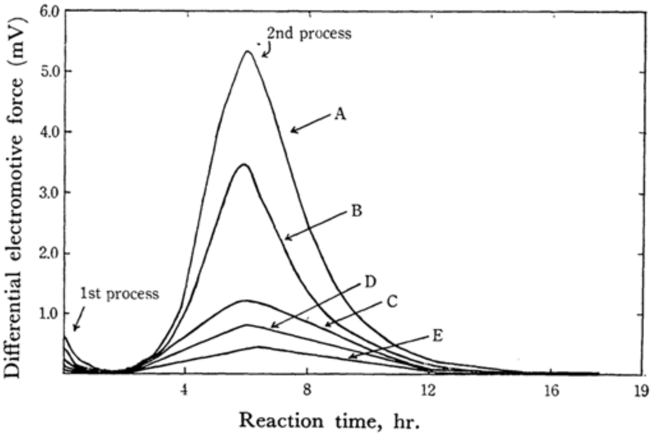

Fig. 4. Recorded curves at the hydration of calcium orthoplumbate.

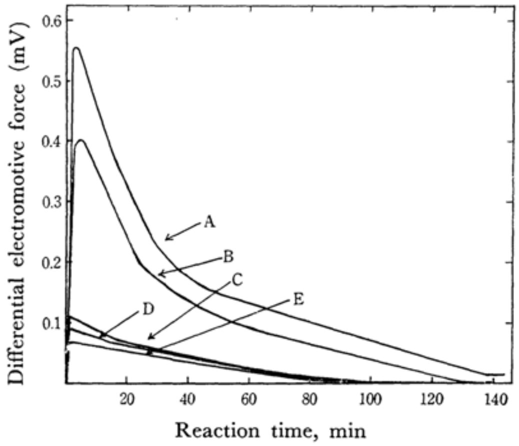

Fig. 5. Recorded curves in the first process at the hydration of calcium orthoplumbate.

the heat liberated in the process of hydrating calcium orthoplumbate is carried out at 20°C. In the hydration of calcium orthoplumbate, the recorded curves which have two maxima corresponding to to the first and the second exothermic processes of hydration are shown in Figs. 4 and 5.

Table I lists the heats of hydration in each process separately. The values of the total heat evolved in the two processes are proportional to the weight of the calcium orthoplumbate specimens; it was about 53.36 cal./g. This proportionality can be explained on the assumption that only a part of the water reacted with calcium orthoplumbate, while the rest of the water did not take part in the hydration reaction.

The X-ray diffraction of the solid, which was filtered off after the first process, did not show the presence of the hydrate of calcium orthoplumbate, as Fig. 6 shows. This suggests that the first process is the immersion and dissolution of calcium orthoplumbate, and that it does not involve the hydration process.

Zettlemoyer[4] observed that the heat of immersion of a solid in various butyl derivatives forms a nearly linear plot against the dipole moment of the functional group in the wetting liquid, and that the slope of the line can be used as a measure of the polarity of the solid. By Zettlemoyer's treatment, the polarity of calcium orthoplumbate can be shown to be as small as that of Teflon and Graphon. In fact, the heats of immersion of calcium orthoplumbate in *n*-butyl alcohol* and *n*-butyric acid* are less than 0.035 cal./g. ($1.16\times10^{-6}$ cal./cm$^2$), as is shown in Fig. 7. Considering the small amount of the heat of immersion, the heat evolved in the first process is mainly due to the heat of dissolution of calcium orthoplumbate into water. The heat of dissolution calculated by neglecting the heat of immersion is about 1.14 cal./g. $Ca_2PbO_4$.

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4) A. C. Zettlemoyer, J. J. Chessick and C. H. Hollabaugh, *J. Phys. Chem.*, **62**, 489 (1958).

* Reagents: commercial extra pure.

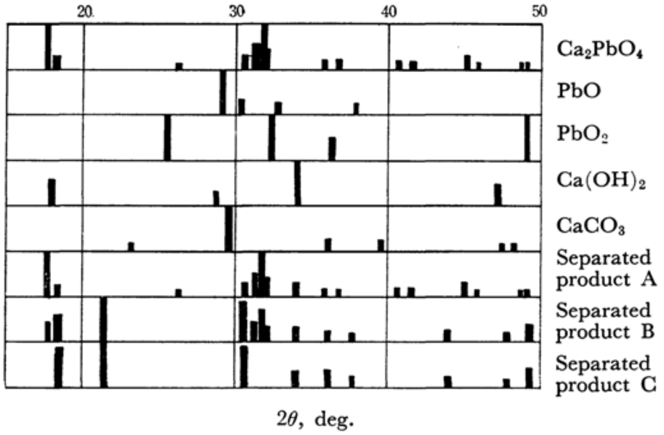

Fig. 6. X-ray diffraction patterns of anhydrous and hydrated calcium orthoplumbate, and reference samples.
Separated product A: after the first process
Separated product B: intermediate one during the second process
Separated product C: after the second process

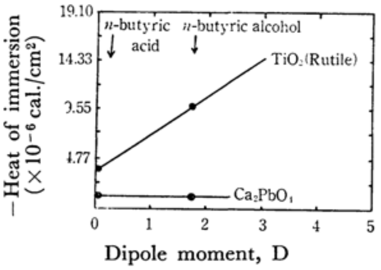

Fig. 7. Heat of immersion versus dipole moment relation for calcium orthoplumbate and titanium dioxide (rutile).

**Analysis of the Second Process.** — After the immersion and dissolution of calcium orthoplumbate have been completed, the second process (the hydration process) is followed by the X-ray diffraction of the solid, as is shown in Fig. 6. The growth of the peaks of the hydrate with the lapse of the hydration time is evident in this figure. Assuming that water rapidly reaches the surface of calcium orthoplumbate through its hydrated layer, and that the rate of the second process is proportional to the surface area of calcium orthoplumbate as a spherical particle, the following relation holds:

$$\mathrm{d}x/\mathrm{d}t = k\cdot n\cdot s \tag{5}$$

where $x$ is the amount of hydration at $t$ min. per gram of calcium orthoplumbate; $s$, the area of the calcium orthoplumbate surface at $t$ min., and $n$, the number of particles per gram of calcium orthoplumbate.

If the reaction proceeds uniformly on the spherical particles with the diameter $a$, including the hydrated layer with thickness of $\Delta/2$, as is shown in Fig. 8, $s$ is given by:

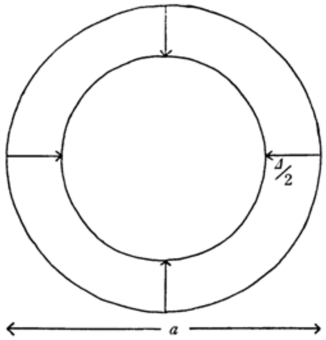

Fig. 8. Simplified model for hydration of calcium orthoplumbate with water.

$$s = 4\pi(a-\Delta)^2/4 = \pi(a-\Delta)^2 \tag{6}$$

When the reaction is completed, $t\rightarrow\infty$ and $x\rightarrow x_\infty$; then we have:

$$\frac{4/3\cdot\pi(a/2)^3\cdot n}{4/3\cdot\pi\{(a-\Delta)/2\}^3\cdot n} = \frac{a^3}{(a-\Delta)^3} = \frac{x_\infty}{x_\infty - x} \tag{7}$$

Taking account of Eq. 7, $s$ is given by:

$$s = \pi\cdot a^2\cdot\{(x_\infty - x)/x\ \}^{2/3} \tag{8}$$

The $n$ value is expressed in terms of density, $\rho$, as:

$$n = \frac{1}{4/3\cdot\pi(a/2)^3\cdot\rho} = \frac{6}{\pi\cdot a^3\cdot\rho} \tag{9}$$

From Eqs. 5, 8, and 9, we obtain:

$$\mathrm{d}x/\mathrm{d}t = (6k/a\rho)\cdot\{(x_\infty - x)/x_\infty\}^{2/3} \tag{10}$$

The integration of Eq. 10 gives:

$$-3\{(x_\infty - x)/x_\infty\}^{1/3} = (6k/a\rho x_\infty)\cdot t \tag{11}$$

Thus, the value of $(x_\infty - x)^{1/3}$ may be expected to be proportional to $t$.

In the present experiment the value of $x$ was not measured directly, but it can reasonably be assumed that the value of $x$ is porportional to the value of $Q$, and that the value can be calculated from the following equation:

$$Q = 4.72 \times 10^{-2} \times \Delta T \cdot t + 25.30 \times \Delta T$$

which can be derived by integration of Eq. 1.* Thus, the term $(x_\infty - x)^{1/3}$ may be replaced by $(Q_\infty - Q)^{1/3}$ without any serious error. Figure 9-(a)—(e) show the $(Q_\infty - Q)^{1/3}$ - $t$ plot. The linear relation in Figs. 9-(a)—(e) indicates the general correctness of the assumption that the second process proceeds through the hydrated layer as a 2/3 order reaction.

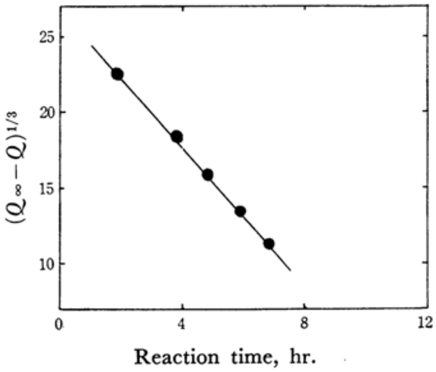

Fig. 9-(a)

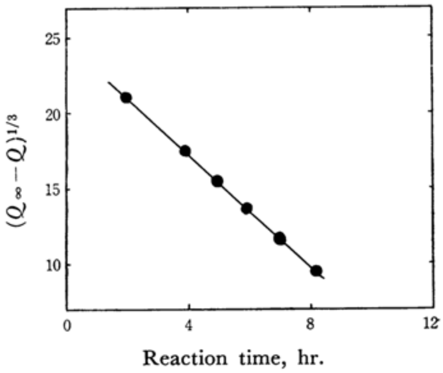

Fig. 9-(b)

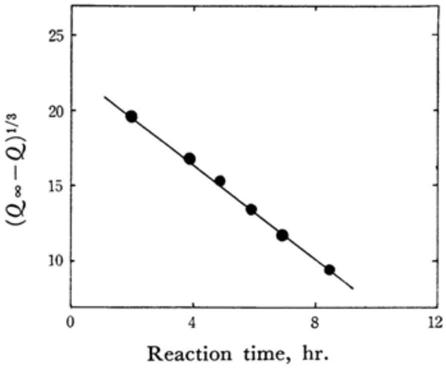

Fig. 9-(c)

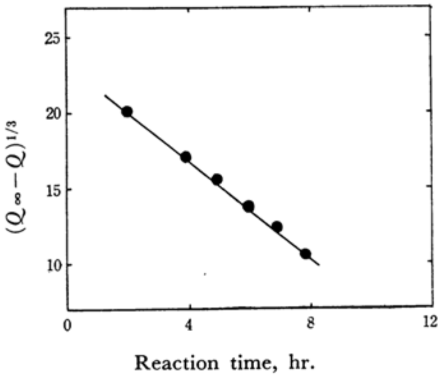

Fig. 9-(d)

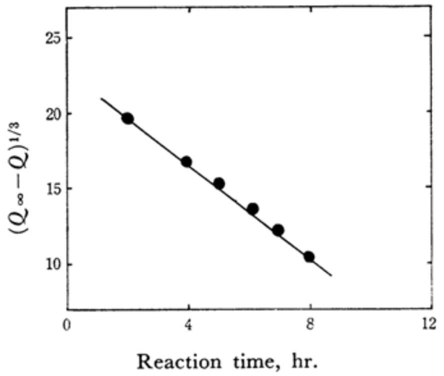

Fig. 9—(e)

Figs. 9-(a)—(e). The relation between the reaction time and $(Q_\infty - Q)^{1/3}$. Molar ratio of $Ca_2PbO_4/H_2O$ are kept (a) = 1/30, (b) = 1/70, (c) = 1/200, (d) = 1/300 and (e) = 1/400.

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* The effective heat capacity, $H$, in Eq. 1 depends, in principle, on the amount of the specimen employed. However, all the $\Delta T$-vs.-time calibration curves coincide for different fillings of the specimen within the precision of the present experimental set-up.