INVESTIGATION OF PEROXYHYDRATES AND HYDRATES
OF RUBIDIUM AND CESIUM CARBONATES.
COMMUNICATION 5. PHYSICOCHEMICAL INVESTIGATION
OF THE BINARY SYSTEMS Rb₂CO₃ - H₂O AND Cs₂CO₃ - H₂O

T. A. Dobrynina and B. S. Dzyatkevich

INORGANIC AND ANALYTICAL CHEMISTRY

The data presented in the literature, on the composition of the crystal hydrates formed in the interaction of rubidium and cesium carbonates with water, are contradictory. Thus, in [1] the existence of two crystal hydrates was established for rubidium carbonate: Rb₂CO₃·1.5H₂O, crystallizing from saturated solutions at 15-20°, and Rb₂CO₃·H₂O, formed in the dehydration of Rb₂CO₃·1.5H₂O at 98°. Recrystallization of cesium carbonate from boiling concentrated alcohol solutions in [2] yielded a compound with the composition 3Cs₂CO₃·10H₂O (or Cs₂CO₃·3.33H₂O). When a saturated aqueous solution of cesium carbonate was evaporated at 15-20°, a crystal hydrate of indefinite composition Cs₂CO₃·(3.5-4)H₂O was obtained [1]. Dehydration of this compound to Cs₂CO₃ at 98° proceeded without the formation of intermediate crystal hydrates [1]. The crystal hydrates of cesium carbonate, isolated in [1] and [2], are evidently identical.

In an investigation of the fusibility in the binary systems Rb₂CO₃ - H₂O [3] and Cs₂CO₃ - H₂O [4], the existence of crystal hydrates of the following compositions was established: Rb₂CO₃·9H₂O, Rb₂CO₃·8H₂O, Rb₂CO₃·1.5H₂O, Rb₂CO₃·0.5H₂O, Cs₂CO₃·8H₂O, Cs₂CO₃·6H₂O, Cs₂CO₃·5H₂O, Cs₂CO₃·3H₂O, Cs₂CO₃·1.5H₂O, and Cs₂CO₃·0.5H₂O. The formation of the compound Cs₂CO₃·5H₂O according to these data corresponded to the metastable state. In an investigation of the solubility in the ternary systems Rb₂CO₃ - H₂O - H₂O and Cs₂CO₃ - H₂O - H₂O at 0° in the region of low hydrogen peroxide concentrations in the liquid phase, the formation of hydrates of the corresponding carbonates was observed [5]. At lower temperatures, in these regions of the ternary systems, the stable solid phase was represented by ice [6]. However, in certain cases, metastable states for hydrated forms of rubidium and cesium carbonates were observed in these regions of the systems.

To establish the composition of the hydrate-type solid phases formed in the ternary systems Rb₂CO₃ - H₂O - H₂O and Cs₂CO₃ - H₂O - H₂O, we investigated the binary systems Rb₂CO₃ - H₂O and Cs₂CO₃ - H₂O.

EXPERIMENTAL

Fusibility in the binary systems Rb₂CO₃ - H₂O and Cs₂CO₃ - H₂O in the low-temperature region was studied by a visual-polythermal method. The solubility in these systems at temperatures above 0° was investigated by an isothermal method.

Determination of the liquidus points in the systems Rb₂CO₃ - H₂O and Cs₂CO₃ - H₂O involved a number of difficulties. Since rubidium and cesium carbonates possess high solubility in water, when the method of gradual addition of weighed samples of these salts to water or to their solutions was used, for the entire investigated concentration interval, the crystallization had to be observed in small volumes of the solutions. The constantly observed supercooling and complete solidification of these solutions made an exact determination of the liquidus and solidus points impossible. Therefore, the liquidus points were determined for aqueous solutions of rubidium and cesium carbonates of various concentrations, obtained by the gradual addition of water to concentrated solutions. In this case, an investigation of the process of crystallization in the systems Rb₂CO₃ - H₂O and Cs₂CO₃ - H₂O within substantial concentration ranges could be conducted in rather large volumes, using comparatively small amounts of these expensive salts.

The content of rubidium and cesium carbonates in the initial concentrated solutions was determined by chemical analysis. The compositions of the solutions obtained in the process of dilution with definite

N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences of the USSR.
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 723–727, April, 1967.
Original article submitted April 23, 1965.
quantities of water were determined by calculation. A periodic analytical monitoring of the composition of the solutions indicated good coincidence of the calculated data with the data of chemical analysis.

The investigation of the process of crystallization of solutions of Rb$_2$CO$_3$ and Cs$_2$CO$_3$ was conducted in double-walled test tubes, equipped with a mixer and thermocouple. For gradual cooling, the test tube with the solution was set up in a Dewar flask over liquid nitrogen. The crystallization point was measured with a copper-constantan thermocouple, connected to a millivoltmeter. The value of the thermocurrent was regulated by a battery of resistors, connected into the circuit of the thermocouple. For the liquidus points, we used the average between the temperatures of appearance and disappearance of crystals.

The solubility of rubidium and cesium carbonates was determined in the temperature interval 0–50°C according to the procedure that we had described previously [7].

The data of an investigation of the binary systems Rb$_2$CO$_3$–H$_2$O and Cs$_2$CO$_3$–H$_2$O are presented in Tables 1 and 2 and on the diagrams of Figs. 1 and 2. The solubility polytherms of these systems within the concentration interval of the corresponding carbonates from 0 to 75% are represented by three branches, corresponding to the formation of the following solid phases: ice and two crystal hydrates of rubidium and cesium carbonates. The following possible compositions had earlier been proposed for the hydrates of rubidium and cesium carbonates: M$_2$CO$_3$·(5–6)H$_2$O and M$_2$CO$_3$·(3–4)H$_2$O [6]. As was shown by further investigations, compounds with the composition M$_2$CO$_3$·3H$_2$O represent the stable hydrate form for rubidium and cesium carbonates within the temperature interval 0–50°C. The higher crystal hydrates of rubidium and

<table>
<thead>
<tr>
<th>Rb$_2$CO$_3$ content in solution, wt. %</th>
<th>Temperature, °C</th>
<th>Solid phase</th>
<th>Rb$_2$CO$_3$ content in solution, wt. %</th>
<th>Temperature, °C</th>
<th>Solid phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.14</td>
<td>4.5</td>
<td>Ice</td>
<td>54.00</td>
<td>8.5</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>14.83</td>
<td>5.5</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18.54</td>
<td>4.3</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.37</td>
<td>5.0</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22.01</td>
<td>3.0</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24.38</td>
<td>1.5</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34.93</td>
<td>1.0</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>43.52</td>
<td>0.0</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45.25</td>
<td>10.0</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47.29</td>
<td>11.0</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>48.37</td>
<td>12.5</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50.26</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>52.56</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31.12</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32.38</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34.25</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36.12</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38.01</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39.85</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41.76</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>43.70</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45.65</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47.59</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>49.53</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>51.48</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>53.43</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>55.38</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>57.33</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>59.28</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>61.23</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>63.18</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65.13</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>67.08</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>69.03</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>71.04</td>
<td></td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 2.** Data of Liquidus and Solidus Points for the System Cs$_2$CO$_3$–H$_2$O

<table>
<thead>
<tr>
<th>Cs$_2$CO$_3$ content in solution, wt. %</th>
<th>Temperature, °C</th>
<th>Solid phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>Ice</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>1.5</td>
<td>1.5</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>2.5</td>
<td>2.5</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>3.0</td>
<td>3.0</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>3.5</td>
<td>3.5</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>4.0</td>
<td>4.0</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>4.5</td>
<td>4.5</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>5.0</td>
<td>5.0</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>5.5</td>
<td>5.5</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>6.0</td>
<td>6.0</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>6.5</td>
<td>6.5</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>7.0</td>
<td>7.0</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>7.5</td>
<td>7.5</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>8.0</td>
<td>8.0</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>8.5</td>
<td>8.5</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>9.0</td>
<td>9.0</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>9.5</td>
<td>9.5</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>10.0</td>
<td>10.0</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>10.5</td>
<td>10.5</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>11.0</td>
<td>11.0</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>11.5</td>
<td>11.5</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>12.0</td>
<td>12.0</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
<tr>
<td>12.5</td>
<td>12.5</td>
<td>Rb$_2$CO$_3$·4H$_2$O</td>
</tr>
</tbody>
</table>

**Fig. 1.** Fusibility diagram of the binary system Rb$_2$CO$_3$–H$_2$O.

**Fig. 2.** Fusibility diagram of the binary system Cs$_2$CO$_3$–H$_2$O.