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Abstract

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ON THE INFLUENCE OF IMPURITIES ON THE DISSOCIATION OF CADMIUM CARBONATE

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As early as 1911, Partington (^{1}) drew attention to the fact that the flow method gives a higher vapor pressure of a crystalline hydrate than do static methods. A detailed study led Partington to the view that this phenomenon is explained by the formation, during dehydration, first of a metastable phase of a lower hydrate or of an anhydrous salt. The same opinion was held by Gjöttig (^{2}), Lewinter and Slonim (^{3}). K. G. Khomyakov established experimentally that crystalline hydrates of zinc, copper, and manganese sulfates give different heats of dehydration depending on the conditions under which the salts are obtained, and explained this phenomenon by the presence of unstable pseudostructures. A case is also known (^{5}) in which a metastable pseudostructure passes, at higher temperatures, into the stable structure of an anhydrous salt. Thus, the β-hemihydrate of calcium sulfate is dehydrated at 180°, and only above 320° does the crystal lattice rearrange into the anhydrite lattice.

As our investigations have shown, the values of the dissociation pressure of many crystalline hydrates, determined by the thermographic method or established by other dynamic methods, coincide or are close in value, whereas isothermal investigations give other values for the dissociation pressure. An analogous result was noted in the work of L. G. Berg and I. S. Rassonskaya (^{6}). The authors suggested that such a discrepancy cannot be explained by overheating or by inaccuracy of the determination itself; its cause should be sought in the different nature of the solid substances participating in the reaction.

Table 1

Pure salt	Pure salt	Salt with addition of AgCl or NaCl	Salt with addition of AgCl or NaCl	Salt with addition of CdO of periclase structure	Salt with addition of CdO of periclase structure
Pressure, mm Hg	Temperature, °C	Pressure, mm Hg	Temperature, °C	Pressure, mm Hg	Temperature, °C
20	256	25	308	50	314
50	380	50	340	100	325
90	390	110	348	250	332
252	413	309	362	400	340
450	425	470	368		
750	435	750	375	750	356

A particularly large discrepancy in the temperatures and pressures of dissociation measured by the static and thermographic methods is observed for cadmium carbonate. According to the data of a study by the static method carried out by Andrusov and Zenthershwer (^{7}), the dissociation temperature of $CdCO_3$ at atmospheric pressure is 90° lower than the decomposition temperature found by Berg and Rassonskaya using thermography (^{8}). By adding 1-2% NaCl, the latter authors succeeded in lowering the dissociation temperature of the salt, but not so much that it coincided completely with the data of Andrusov and Zenthershwer.

Having assumed that table salt, whose structure is very close to the structure of cadmium oxide, affects the equilibrium of the decomposition process, we set ourselves the task of selecting such an additive by means of which it would be possible to shift the reaction equilibrium toward the formation of a stable dissociation product. In choosing the additive, we were guided by the principle of crystallochemical correspondence between the introduced impurity and the dissociation product.

On the heating curves of freshly precipitated carbonate, recorded at different pressures, one endothermic effect is observed, corresponding to the dissociation of $CdCO_3$. Its temperature increases with increasing pressure, reaching 435° at 750 mm Hg (Table 1). These data are in good agreement with the results of the study by Berg and Rassonskaya. Our experiments also showed that the same effect as NaCl on the decomposition of cadmium carbonate is exerted by silver chloride, which is in close crystallochemical relationship with table salt. Potassium chloride, however, whose crystal-lattice parameters differ by more than 15% from the lattice parameters of NaCl, has no effect at all on the dissociation process of cadmium carbonate.

Fig. 1

As was to be expected, the greatest lowering of the decomposition temperature

Fig. 1

Figure 1: Fig. 1

of the carbonate under study was obtained by introducing an impurity of stable cadmium oxide (Table 1). Moreover, not every cadmium oxide causes a decrease in the carbonate dissociation temperature, but only CdO obtained as a result of the decomposition of $CdCO_3$ with 2-3% NaCl and calcined at 500-600°. The oxide obtained in this way lowers the dissociation temperature of $CdCO_3$ to values fairly close to the data of Andrusov and Centerszwer (Fig. 1). It is very important to note that, regardless of the amount of impurity introduced, the lowering of the dissociation temperature remains constant; however, the method of placing the impurity into the dissociating phase proves to be a very essential factor. If the impurity is introduced without thoroughly mixing it with the dissociating substance, no effect may be obtained. In our opinion, both these facts support the supposition that the role of the additives is reduced to stimulating the formation of a stable dissociation product.

We also carried out a thermodynamic treatment of the data on the dissociation pressure of cadmium carbonate obtained by the thermographic method. From the values of the dissociation temperatures at different pressures given in Table 1, a diagram was constructed in the coordinates $\lg P–1000/T$ (Fig. 1). Line I corresponds to the dissociation of cadmium carbonate without an additive, line II to the decomposition of the carbonate with 2-3% sodium chloride or silver chloride, and line III to the dissociation of $CdCO_3$ with an impurity of CdO of the periclase structure.

The rectilinearity of the dependence $\lg P–1000/T$ makes it possible, by extrapolation, to find the dissociation pressure at 298° K. In view of the fact that at low pressures (< 1.5 atm) the equilibrium constant of the dissociation process can be expressed by the equation: $K_a = K_p + P^n$, where n is the number of molecules of the gaseous dissociation product, it is legitimate to assume that $P_{298} = K_{p\,298}$. Hence, using the second approximate Nernst equation:

$$\lg K_p = -\frac{\Delta H_{298}}{4.575T} + \Delta n \cdot 1.75 \lg T + i,$$

we calculate the heat of decomposition in all three cases (i is the conventional chemical constant, Δn is the change in the number of molecules of the gaseous product). From the isotherm of the chemical reaction, $\Delta Z^0 = -RT \ln K_p$, the free energy of the reaction was calculated.

thermal dissociation of the pure salt, as well as of the carbonate with additions of NaCl, AgCl, and CdO.

Our calculations showed (Table 2) that the greatest heat of decomposition belongs to the dissociation of the pure carbonate (43.96 kcal). The addition of

NaCl or AgCl lowers the heat of decomposition to 36.46 kcal, and an admixture of stable cadmium oxide lowers it to 25.91 kcal. The latter value of the heat of dissociation is very close to the thermal effect calculated with the aid of standard heats of formation of the reaction components (25.61 kcal).

Table 2

	Pure saltCdCO$_3 \rightleftarrows$ CdO + CO$_2$	CdCO$_3$ with an admixture of NaCl$\rightleftarrows$ CdO + CO$_2$	CdCO$_3$ with an admixture of CdO$\rightleftarrows$ CdO + CO$_2$
$-\lg K_p^{298}$ (mm)	23.8	18	10.93
ΔZ^0_{298}	108.885	82.35	50.0047
ΔH_{298} (kcal)	43.96	36.46	25.91

The difference in the heats of decomposition of the pure salt and of cadmium carbonate with an addition of stable oxide makes it possible to calculate the heat of transition of the metastable oxide into the stable one (-18.05 kcal), as well as the heat of formation of metastable cadmium oxide ($-62.36+(-18.05) = -80.41$ kcal), where -62.36 kcal is the heat of formation of the stable modification (^8).

Thus, the results obtained by us in studying the process of thermal dissociation of cadmium carbonate showed that great caution is required in assessing discrepancies in data for the determination of dissociation pressure carried out by static and thermographic methods. The cause of these discrepancies should not always be sought in overheating or in measurement inaccuracies that occur in the study of processes by dynamic methods. Sometimes the discrepancy may be caused by the formation, in the course of the reaction, of a pseudostructure which, according to Slonim (^3), possesses a longer lifetime than the reaction rate. In studies by static methods, owing to the slowness with which equilibrium is established, the aging process also proceeds simultaneously, as a result of which a stable form is obtained. In the dynamic method of investigation, however, as a result of the rapid course of the process, the solid phase formed during dissociation does not have time to acquire a stable structure. By introducing seed crystals of the stable dissociation product, however, it is possible to shift the reaction equilibrium toward the formation of the stable phase.

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