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DEAQUATION KINETICS AT THE BOILING POINT OF WATER: $BaCl_2 \cdot 2H_2O$ AND $BaBr_2 \cdot 2H_2O$*

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SUMMARY

An equation is derived which describes the non-isothermal mass-loss kinetics of a deaquation reaction which occurs near the boiling point of water. The equation is tested using published experimental mass-loss data for the deaquation of $BaCl_2 \cdot 2H_2O$ and $BaBr_2 \cdot 2H_2O$.

INTRODUCTION

The thermal deaquation reactions of $BaCl_2 \cdot 2H_2O$ and $BaBr_2 \cdot 2H_2O$ have been investigated by a number of workers[1-10]. For both salts, the first water molecule is evolved near the boiling point of water. It has been established that the mono-hydrate salts coexist with liquid water (saturated salt solution) over a narrow temperature range following the release of the first water of hydration[2,10]. It may therefore be expected that the mass-loss kinetics for the evolution of the water is controlled by the vaporization of the liquid water at its boiling point. The water is probably present in the sample as a thin film covering the solid salt particles. In this investigation, non-isothermal kinetic equations for the vaporization of thin layers of water at the boiling point of water were derived and tested experimentally by studying the deaquation reactions of $BaCl_2 \cdot 2H_2O$ and $BaBr_2 \cdot 2H_2O$.

THEORETICAL CONSIDERATIONS

Liquid water, which is released in a non-isothermal deaquation reaction near its boiling point, will vaporize and maintain a constant temperature. Consider a thin layer of water coating the solid particles at the boiling point of the solution in a furnace whose temperature is increasing in a linear manner. The heat change of the water in time, dt, due to heat transfer from the furnace should be proportional to the heat difference between the water and the furnace, ΔT, and to the surface area of the water. For water distributed as a thin film, the surface area of the water is approximately proportional to the number of moles, η, of water present. The heat content change due to the vaporization of the water in time, dt, is $\Delta H d\eta$, where ΔH is the

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enthalpy of vaporization of water and $d\eta$ is the number of moles of water evolved in time, dt. Hence, the total heat content change of the solution, dq, in time, dt, is

$$dq = \gamma \Delta T \eta \, dt + \Delta H \, d\eta \tag{1}$$

where γ is a constant of proportionality. At any time during the vaporization of the water the total heat content of the solution is given by

$$q = C_P T_B \eta \tag{2}$$

where C_P is the heat capacity of the solution at constant pressure and T_B is the boiling point of the saturated aqueous solution. Differentiation of Eqn. (2) gives

$$dq = C_P T_B \, d\eta \tag{3}$$

Equating Eqns. (1) and (3) gives

$$C_P T_B \, d\eta = \gamma \Delta T \eta \, dt + \Delta H \, d\eta \tag{4}$$

The temperature difference, ΔT, is given by

$$\Delta T = T_f - T_B \tag{5}$$

where T_f is the linearly increasing furnace temperature which increases according to

$$\frac{dT_f}{dt} = \beta \tag{6}$$

where β is the heating rate.

Rearranging, and defining zero time as the time at which $T_f = T_B$, Eqn. (7) may be integrated to give

$$\int_{T_B}^{T_f} dT_f = \beta \int_0^t dt \tag{7}$$

$$T_f = \beta t + T_B \tag{8}$$

Therefore,

$$\Delta T = \beta t$$

Eqn. (4) may therefore be written as

$$(C_P T_B - \Delta H) d\eta = \gamma \beta t \eta \, dt \tag{9}$$

or, on rearranging and integrating, making use of the condition that $\eta = \eta_0$ where $t = 0$, the following equation is obtained

$$\ln \frac{\eta}{\eta_0} = \ln \alpha = \frac{\gamma \beta t^2}{(C_p T_B - \Delta H)} \tag{10}$$

where $\alpha = \frac{\eta}{\eta_0}$.

A plot of $\ln \alpha$ *vs.* t^2 should therefore be a straight line with a slope of

$$\frac{\gamma\beta}{(C_P T_B - \Delta H)}.$$

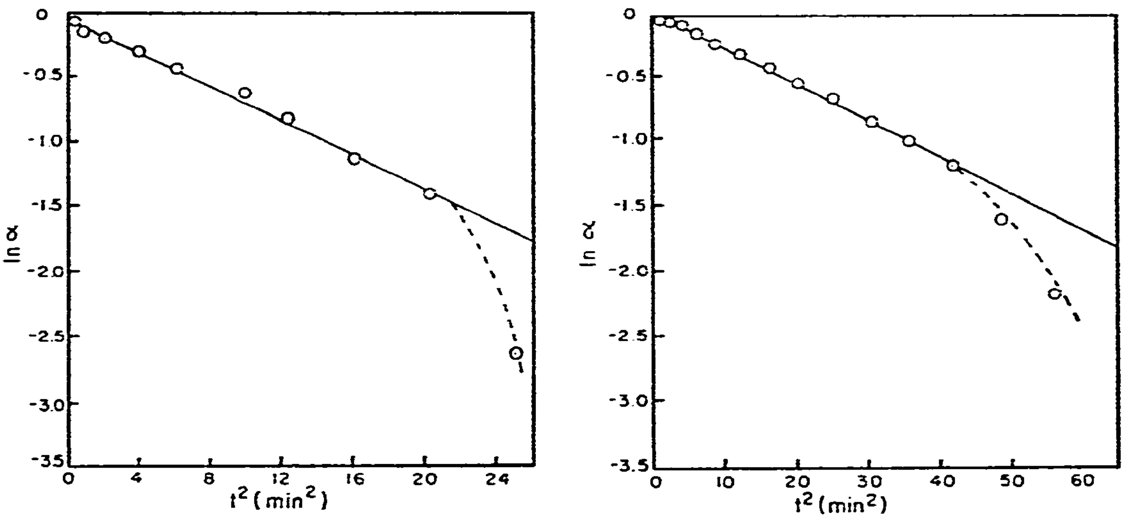

Fig. 1. Plot of $\ln \alpha$ *vs.* t^2 for the deaquation of $BaCl_2 \cdot 2H_2O$. The furnace atmosphere was water-saturated nitrogen and the heating rate was 5°C/min. (Ref. 10).

Fig. 2. Plot of $\ln \alpha$ *vs.* t^2 for the deaquation reaction of $BaBr_2 \cdot 2H_2O$. The furnace atmosphere was water-saturated nitrogen and the heating rate was 5°C/min.

RESULTS

Eqn. (10) was tested by the use of previously published TG data for $BaCl_2 \cdot 2H_2O$ and $BaBr_2 \cdot 2H_2O$ in a water-vapor saturated nitrogen atmosphere and a heating rate of 5°C/min. A plot of $\ln \alpha$ *vs.* t^2 for the deaquation reaction of one water molecule for $BaCl_2 \cdot 2H_2O$ is illustrated in Fig. 1, while that for $BaBr_2 \cdot 2H_2O$ is illustrated in Fig. 2. As can be seen, in both cases the plots were linear until near completion of the evolution of the water, at which time marked deviation from linearity occurred. This deviation probably occurs because, near the end of the reaction, there is only a small amount of water remaining in the sample and the temperature of the furnace is several degrees above the boiling point of the solution. Hence, the water probably vaporizes more rapidly than it can diffuse from the sample and the mass-loss rate is no longer controlled by the rate of vaporization of water.

The values of the slopes of the curves in Figs. 1 and 2 may be used to calculate the values of the proportionality constant, γ, which is the only unknown parameter in Eqn. (10).

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