# THERMAL DECOMPOSITIONS OF FORMATES. PART IV. THERMAL DEHYDRATIONS OF Mg(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) AND Cd(II) FORMATE DIHYDRATES

YOSHIO MASUDA

*General Education Department, Niigata University, Niigata (Japan)*

AND SHUNSUKE SHISHIDO

*Department of Chemistry, Faculty of Science, Niigata University, Niigata (Japan)*

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ABSTRACT

The thermal dehydrations of formate dihydrates of Mg(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were studied by means of thermogravimetry, differential thermal analysis and differential scanning calorimetry in air.

The reaction orders of dehydration obtained by the dynamic and the static methods were found to be 2/3 for all the salts examined, which indicated that the rate of dehydration was controlled by a chemical process at a phase boundary. This was confirmed by microscopic observation.

The values of activation energy, frequency factor and the enthalpy change of dehydration for all salts examined, were 21–30 kcal mole$^{-1}$, $10^{10}$–$10^{12}$ sec$^{-1}$ and 28–31 kcal mole$^{-1}$, respectively.

The temperature at which the dehydration occurred was regarded as a measure of the strength of the metal–$OH_2$ bond, and this temperature increased with increasing the reciprocal of the radius of the metallic ion.

INTRODUCTION

Although the thermal decompositions of formates have been studied extensively, the thermal dehydrations of formate dihydrates and their kinetic and calorimetric parameters are scarcely reported[1-7]. The relations between these parameters have not been examined, because those were obtained under different experimental conditions.

The present paper is a systematical study of the thermal dehydrations of various bivalent metal formate dihydrates by means of thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC).

Basic kinetic constants, such as the order of reaction, the enthalpy change of dehydration, activation energy and frequency factor were determined. In addition,

these kinetic and calorimetric parameters were related to the strength of the metal–$OH_2$ bond and the thermal stabilities of these salts.

When the kinetic study is based on thermogravimetry, two approaches are possible in principle, viz. the static method at a constant temperature and the dynamic method under elevating temperatures. In this study, the results obtained from these two approaches were compared.

EXPERIMENTAL

The bivalent metal formate dihydrates were commercially obtained and re-crystallized from distilled water, except $Cu(HCO_2)_2 2H_2O$, which was obtained by means of very slow evaporation at 328 K, from an aqueous solution containing free formic acid[8].

Each sample was pulverized with pastel and sieved to a narrow fraction of 250–300 mesh size in order to carry out the dehydration process under the same conditions for all the salts.

The TG and DTA curves were simultaneously recorded on a Rigaku Thermo-flex TG–DTA M8075 at a heating rate of 5 K min$^{-1}$ in air. About 10 mg of sample was weighed into an aluminium crucible, and measured by use of $\alpha$-alumina as reference material.

The rate of dehydration was measured using the Rigaku Thermoflex at a constant temperature kept within $\pm$ 0.5 K.

The enthalpy change for dehydration was obtained from the DSC curve recorded on a Rigaku Thermoflex DSC 8055, at a heating rate of 5 K min$^{-1}$. The instrument was calibrated by measuring the heat of transition of $KNO_3$ ($\Delta H = 1.294$ kcal mole$^{-1}$ at 401 K).

RESULTS AND DISCUSSION

The TG and DTA curves of the bivalent metal formate dihydrates are shown in Fig. 1. The temperature range of successive dehydration, the temperature for the peak of the DTA curves ($T_p$), and the weight loss after complete dehydration are listed in Table 1. The smoothness of the curves and agreement between the calculated and observed values of weight loss suggest that dehydration takes place successively as one step reaction after its occurrence, for all the formate dihydrates examined.

The activation energy and the reaction order calculated by the dynamic method of Freeman and Carroll[9] are shown in Table 2. The reaction order seems to be 2/3 for all the salts.

The Coats–Redfern method[10] was used to ensure the validity of this value. Figure 2 shows the Coats–Redfern plots for the dehydration of $Ni(HCO_2)_2 2H_2O$, obtained by assuming the reaction order ($n$) to be 1/2, 2/3 and 1. When $n$ was assumed to be 2/3, the plot gave a straight line to yield the activation energy, 28.06 kcal mole$^{-1}$, which agreed with that obtained by the Freeman–Carroll method, 26.26
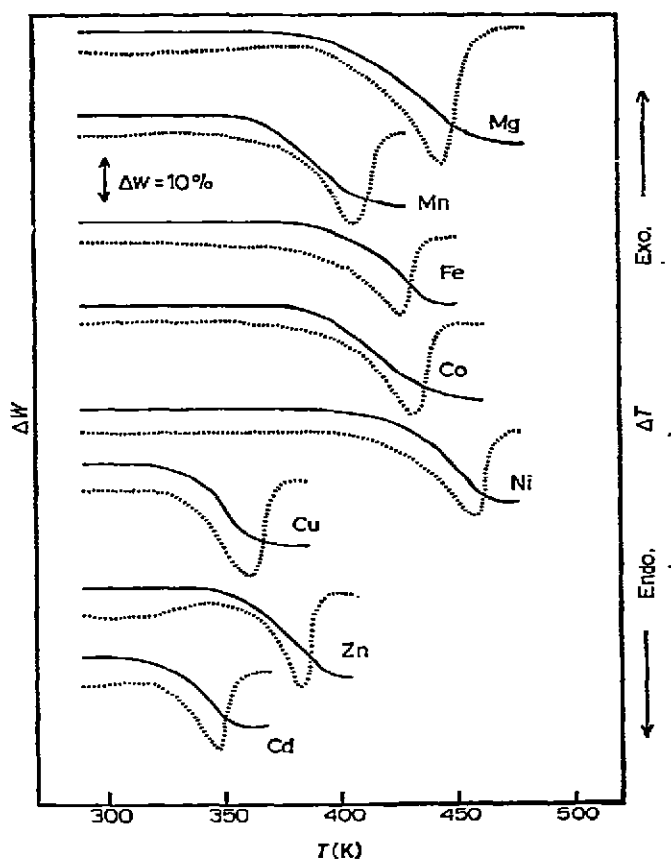
Fig. 1. TG (solid line) and DTA (broken line) for the reaction $M(HCO_2)_2 2H_2O(s) \rightarrow M(HCO_2)_2(s) + 2H_2O(g)$

## TABLE 1

TEMPERATURE RANGE, TEMPERATURE FOR PEAK OF DTA CURVE $(T_p)$ AND WEIGHT LOSS VALUE FOR THE REACTION $M(HCO_2)_2 2H_2O(s) \rightarrow M(HCO_2)_2(s) + 2H_2O(s)$

| M | Temp. range (K) | $T_p$ (K) | Weight loss (%) | |
| --- | --- | --- | --- | --- |
| | | | Calc. | Obs. |
| Mg | 381–458 | 442 | 23.99 | 23.90 |
| Mn | 357–413 | 405 | 19.89 | 19.70 |
| Fe | 370–430 | 415 | 19.79 | 19.88 |
| Co | 372–455 | 432 | 19.46 | 19.09 |
| Ni | 387–476 | 450 | 19.48 | 20.16 |
| Cu | 342–376 | 360 | 18.99 | 18.71 |
| Zn | 343–385 | 383 | 18.81 | 18.80 |
| Cd | 308–351 | 346 | 15.10 | 15.45 |

TABLE 2

REACTION ORDER ($n$), ACTIVATION ENERGY ($E$) AND ENTHALPY CHANGE ($\Delta H$) FOR THE REACTION
$M(HCO_2)_2 2H_2O(s) \rightarrow M(HCO_2)_2(s) + 2H_2O(g)$

| M | n | $E(kcal\ mole^{-1})$ | | $\Delta H$ |
| | | F–C | C–R | $(kcal\ mole^{-1})$ |
| --- | --- | --- | --- | --- |
| Mg | 0.64 | 25.30 | 26.22 | 30.86 |
| Mn | 0.60 | 24.16 | 25.50 | 28.84 |
| Fe | 0.69 | 24.65 | 25.90 | 29.59 |
| Co | 0.65 | 25.47 | 26.70 | 30.46 |
| Ni | 0.76 | 26.26 | 28.06 | 30.55 |
| Cu | 0.61 | 24.46 | 24.65 | 30.56 |
| Zn | 0.68 | 23.90 | 24.54 | 29.53 |
| Cd | 0.68 | 21.80 | 22.77 | 28.38 |
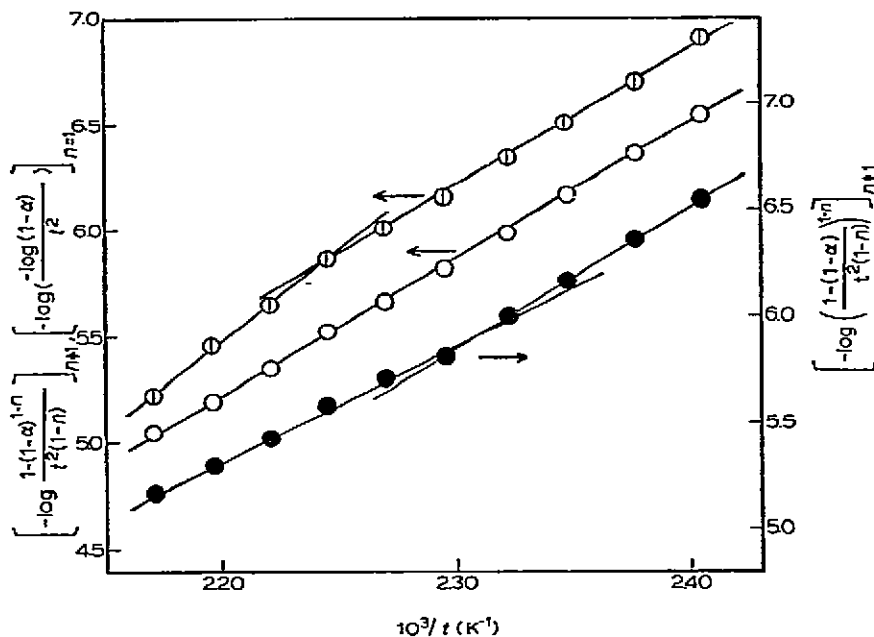


Fig. 2. Plots by the Coats-Redfern method for the reaction $Ni(HCO_2)_2 2H_2O(s) \rightarrow Ni(HCO_2)_2(s) + 2H_2O(g)$. ⊕, $n = 1$; ○, $n = {}^2/_3$; ●, $n = {}^1/_2$.

kcal mole$^{-1}$. These results mentioned above were similar to those for the dehydrations of other formate dihydrates, which indicated that the mechanism of dehydration of these salts must be almost same. This similarity in mechanism for the dehydrations of these salts seems to be ascribable to the similarity of their crystal structures. From X-ray analysis[8, 11-14], it has been found that formate dihydrates of Mg(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) form isomorphous crystals, of which a unit cell includes two metallic ions. One metallic ion is surrounded by six carbonyl oxygen atoms and the other by two carbonyl oxygen atoms and four water molecules, both in a regular octahedron form.
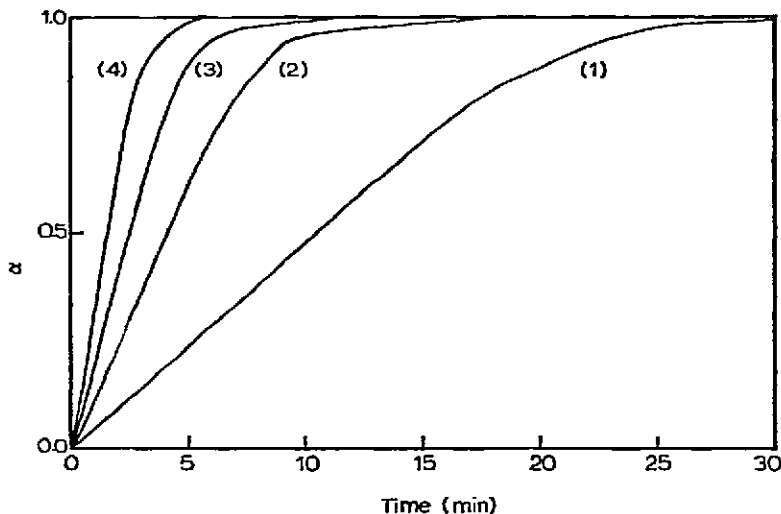
Fig. 3. $\alpha(t)$ curves for $Fe(HCO_2)_22H_2O$. (1) 401 K; (2) 410 K; (3) 420 K; (4) 426 K.
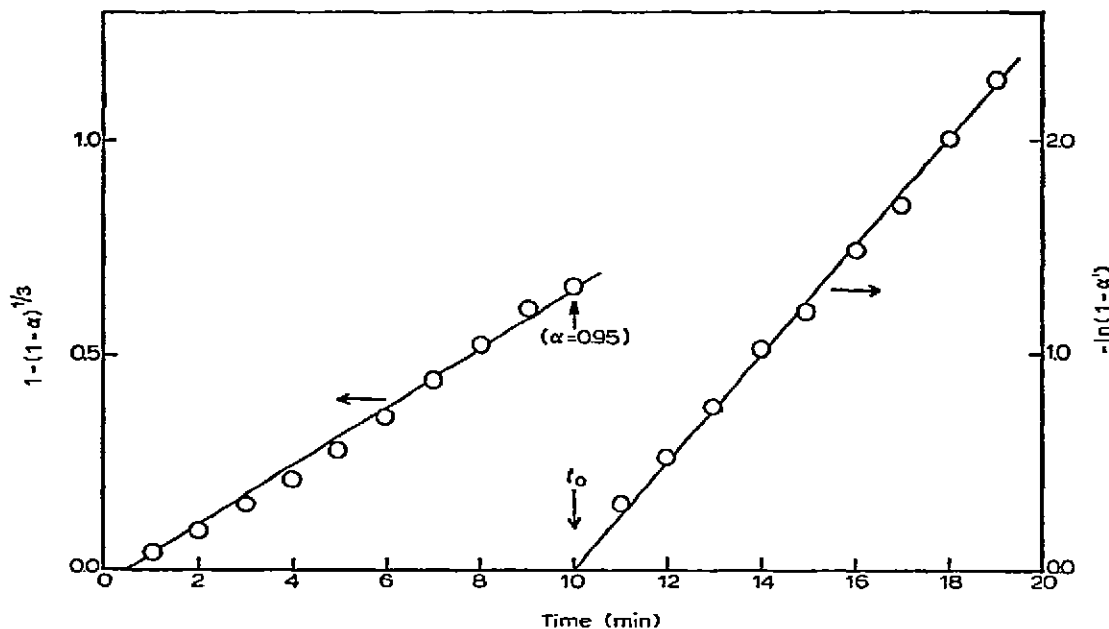


Fig. 4. Plots of $1 - (1 - \alpha)^{1/3}$ vs. time and $\ln(1 - \alpha')$ vs. time for $Fe(HCO_2)_22H_2O$ at 410 K.

The relation between the fraction of dehydration ($\alpha$) and time of reaction ($t$) for the isothermal dehydration of $Fe(HCO_2)_22H_2O$ are shown in Fig. 3. The dehydration in the range $0 < \alpha < 0.95$ obeyed the phase boundary controlled expressed[15]

$$1 - (1 - \alpha)^{1/3} = k_1 t \tag{1}$$

where $k_1$ is a rate constant (Fig. 4). In the range $\alpha > 0.95$, the dehydration obeyed the unimolecular decay expression[15]

$$-\ln(1 - \alpha') = k_2(t - t_0) \tag{2}$$

TABLE 3

ACTIVATION ENERGY $(E)$ AND FREQUENCY FACTOR $(A)$ OBTAINED BY ISOTHERMAL EXPERIMENT FOR THE REACTION $M(HCO_2)_2 2H_2O(s) \rightarrow M(HCO_2)_2(s) + 2H_2O(g)$

| M | Phase boundary controlled process | | Unimolecular decay process | |
|---|---|---|---|---|
| | $E_1(kcal\ mole^{-1})$ | $A_1\ (sec^{-1})$ | $E_2(kcal\ mole^{-1})$ | $A_2\ (sec^{-1})$ |
| Mg | 25.29 | $1.31 \cdot 10^{10}$ | 33.96 | $1.40 \cdot 10^{15}$ |
| Mn | 25.01 | $7.17 \cdot 10^{12}$ | 36.28 | $2.65 \cdot 10^{18}$ |
| Fe | 24.90 | $1.13 \cdot 10^{10}$ | 38.10 | $7.38 \cdot 10^{17}$ |
| Co | 26.89 | $2.51 \cdot 10^{10}$ | 30.81 | $2.46 \cdot 10^{15}$ |
| Ni | 26.51 | $1.20 \cdot 10^{10}$ | 33.80 | $5.53 \cdot 10^{15}$ |
| Cu | 24.59 | $8.35 \cdot 10^{12}$ | 30.90 | $2.20 \cdot 10^{17}$ |
| Zn | 23.88 | $1.77 \cdot 10^{11}$ | 34.89 | $3.28 \cdot 10^{18}$ |
| Cd | 21.01 | $1.56 \cdot 10^{11}$ | 28.49 | $2.82 \cdot 10^{16}$ |

where $\alpha'$ is $(\alpha - 0.95)/(1 - 0.95)$, $k_2$ is a rate constant for the unimolecular decay process and $t_0$ is the time when $\alpha$ becomes 0.95 (Fig. 4). The results obtained from the isothermal experiments for the other formate dihydrates were similar to those for $Fe(HCO_2)_2 2H_2O$, which proceeded through the two processes. Activation energies and frequency factors obtained from the isothermal dehydrations are shown in Table 3. The activation energies for the phase boundary controlled process gave good agreement with that obtained by the dynamic method. The activation energy for the unimolecular decay process was somewhat larger than that of the phase boundary controlled process.

It is most improbable that the dehydration process suddenly changes from that described by the phase boundary controlled formula to that by unimolecular decay when the fraction of dehydration reaches about 0.95. This transition from the former to the latter process may be interpreted as follows. In the range $\alpha > 0.95$ the dehydration process must essentially obey the phase boundary controlled formula, and the dehydration proceeds rapidly from its dehydrated surroundings to the center of the powdered specimen. Consequently, it appears that the dehydration process at the final stage obeyed the unimolecular decay formula.

The most reasonable reaction order obtained by the dynamic method was 2/3, hence the kinetic equation may be written in the following form

$$d\alpha/dt = k(1 - \alpha)^{2/3} \qquad (3)$$

where $\alpha$ is the fraction of dehydration, $k$ is the rate constant of the dehydration and $t$ is the time of reaction. The integrated form of eqn. (3) is consistent with eqn. (1). These results obtained by the dynamic and the static methods indicate that the dehydrations of formate dihydrates begin on the surface of crystals and propagate to their centers. This was confirmed by microscopic observation. Figure 5 shows the microscopic photographs of $Cd(HCO_2)_2 2H_2O$, partially dehydrated, and $Cd(HCO_2)_2$-

0.5mm
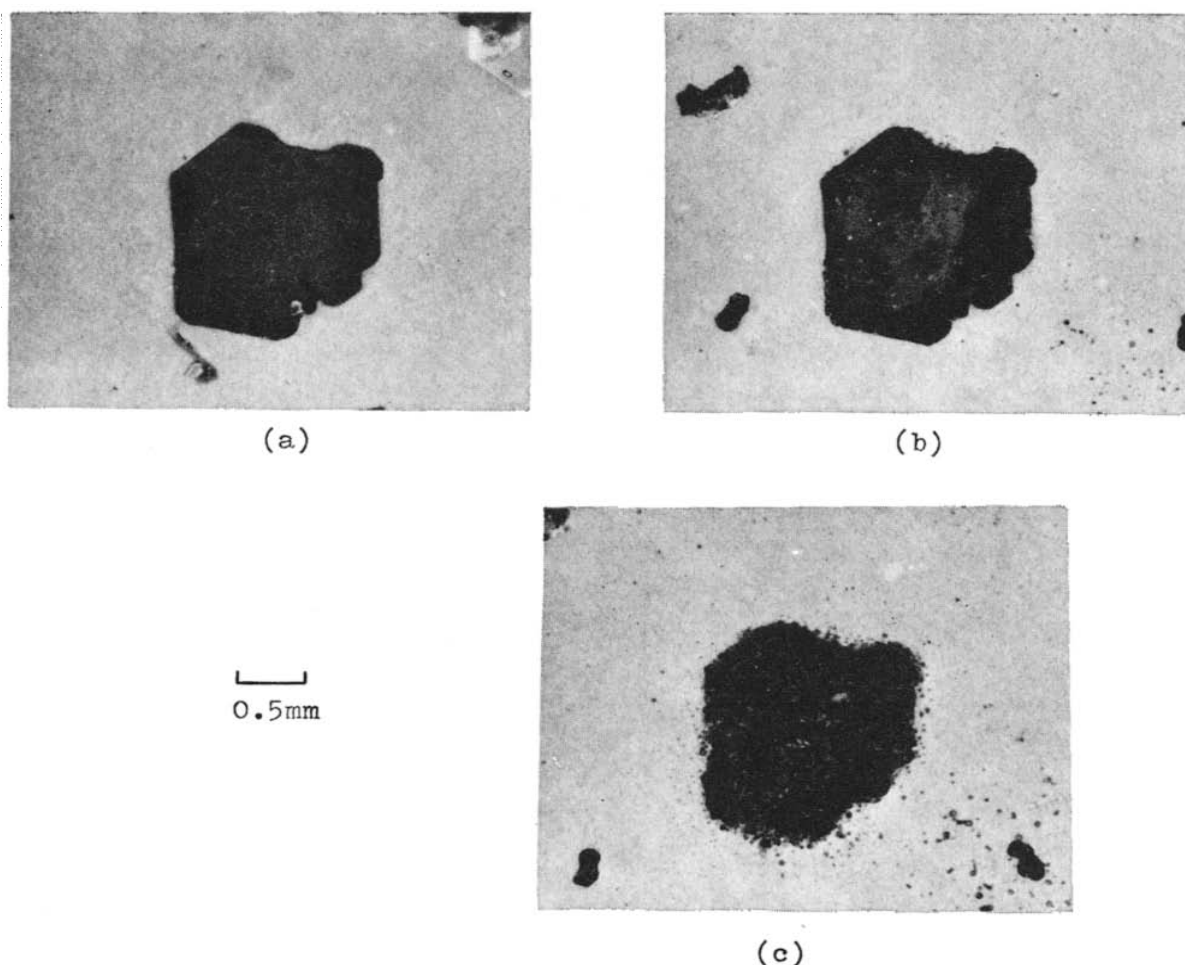
Fig. 5. Microphotographs of (a) Cd(HCO₂)₂2H₂O; (b) partially dehydrated Cd(HCO₂)₂2H₂O heated at 358 K for 4 min; (c) Cd(HCO₂)₂.

$2H_2O$. It is apparent that the dehydration proceeds from the outer to the inner surface of the particle.

The activation energy ($E$) for the dehydration of these salts must be generally recognized as the energy which is necessary to activate the $M-OH_2$ bond, therefore, it may be related to the strength of the $M-OH_2$ bond. The relation between the temperature at which the weight loss begins ($T_i$) and $E$ shows a linearity, which suggests that $T_i$ can be regarded as a measure of the strength of the $M-OH_2$ bond (Fig. 6).

If the strength of the $M-OH_2$ bond is assumed to be dependent on the electrostatic force between the metallic ion and the lone pair electrons in the water molecule, $T_i$ must be related to the reciprocal of the radius of the metallic ion ($1/r_M$). In Fig. 7, the relation between $T_i$ and $1/r_M$ shows a roughly linearity, which means that the $M-OH_2$ bond tends to have electrostatic character. A similar relation between $T_i$ and $1/r_M$ for the dehydration of oxalate dihydrates[16] could be found, as shown in Fig. 7.

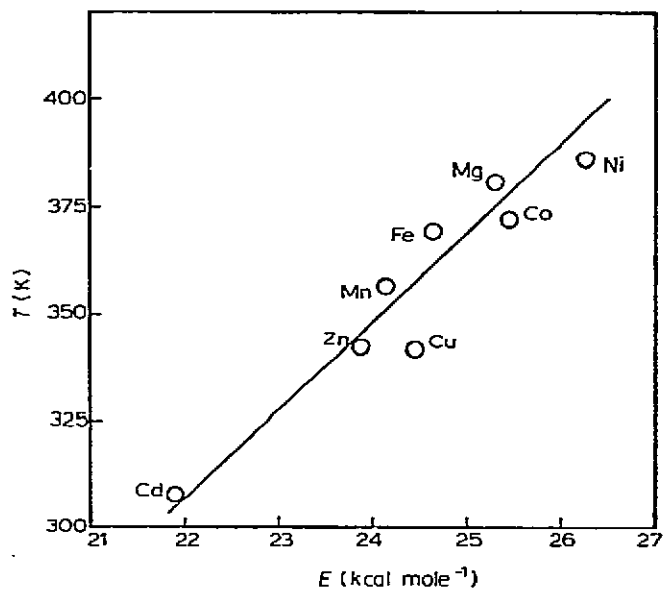$T_i$'s of Cu(II), Zn(II) and Cd(II) salts, of which metallic ions have an electronic

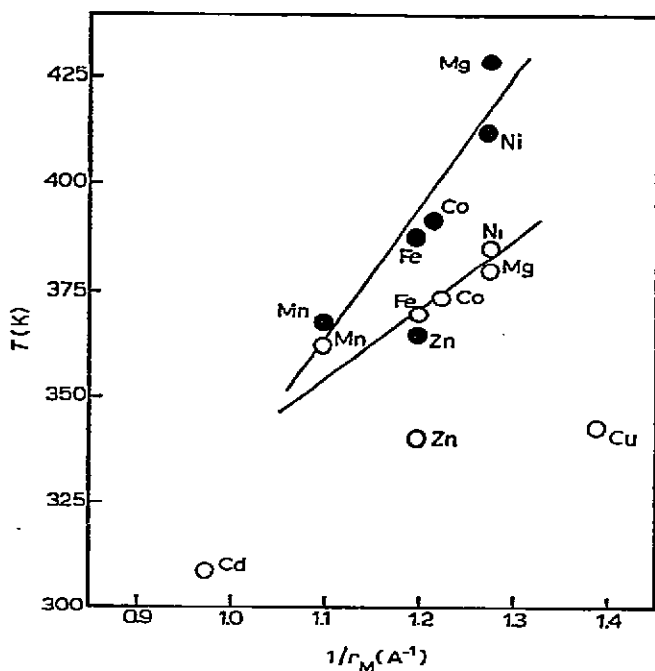Fig. 6. Relationship between $T_1$ and $E$. The values of $E$ were obtained by the Freeman–Carroll method.



Fig. 7. Relationship between $T_1$ and $1/r_M$ (Goldschmidt's value). $\bigcirc$, $M(HCO_2)_2 2H_2O(s) \rightarrow M(HCO_2)_2$ (s) $+ 2H_2O(g)$; $\bullet$, $MC_2O_4 2H_2O(s) \rightarrow MC_2O_4(s) + 2H_2O(g)$.

structure with completely, or almost completely, filled $d$ orbitals, were lower than the expected values based on their ionic radii.

The enthalpy changes ($\Delta H$) for the dehydrations are shown in Table 3. For the transition metal group (from Mn to Zn), $\Delta H$ increased in the order: Mn < Fe < Co < Ni $\sim$ Cu > Zn. Roughly speaking, the stabilities of these salts increase in this order,

which is almost parallel to that of Irving-Williams. Comparison of $T_i$ with $\Delta H$ revealed a roughly linear relation between them.

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