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THE INFLUENCE OF THE ENVIRONMENT ON THE THERMAL DECOMPOSITION OF OXYSALTS*

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The environment can influence the thermal decomposition of an oxysalt by;

(a) causing a change in the course of chemical decomposition

or

(b) causing an alteration in the physical nature of the solid product or solid intermediates.

The environment can also effect the equilibrium condition or the course of the kinetics. The use of special techniques such as thermogravimetry, differential thermal analysis, or differential scanning calorimetry to study the decomposition means that a special environment is imposed on the oxysalt and this effects the thermal decomposition process.

The influence of the environment in changing the course of a chemical reaction can be illustrated by reference to the decomposition of zinc oxalate and nickel oxalate. The DTA shows that the decompositions are endothermic in inert atmospheres but exothermic in air or oxygen. The reasons are different however in each case. Thus although the product of decomposition of zinc oxalate is zinc oxide the change in character of the decomposition from endothermic to exothermic is due to the catalytic oxidation of carbon monoxide to carbon dioxide in the presence of oxygen. The similar change in the character of nickel oxalate decomposition is however due to nickel formation in an inert atmosphere but nickel oxide in air or oxygen.

The alteration in the physical nature of the solid products is illustrated by surface area measurements on solid residues from the decomposition of carbonates or oxalates. The kinetic and chemical equilibrium studies showing the influence of environment are illustrated by reference to dehydration studies, carbonate and oxalate decompositions.

The influence of the environment on the course of the thermal decomposition is not always appreciated. This led early workers in the field to claim that oxalate decompositions were exothermic in character whereas it is now quite clear that majority of such decompositions in an inert atmosphere are endothermic [1, 2]. The most obvious change caused by the environment is when the actual product is different due to the influence of the surrounding gas atmosphere. This is illustrated by the different oxide products which arise in the case of manganese oxalate decomposition [3, 4]. The product in vacuum, nitrogen or any other inert gas is

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the green oxide MnO whilst the product in oxygen is one of the other manganese oxides, MnO_2, Mn_2O_3, Mn_3O_4, recognised by their black or brownish-black colour, the exact nature of this product depending on "local" conditions adjacent to the decomposing sample, the container design, and the packing and amount of sample used in the experiment.

However there are other changes in the thermal decomposition process which may not be so obviously apparent. The physical texture of the solid residues may be affected. To investigate such changes can entail the use of optical or electron microscopy as evidenced by the work of Giovanoli [5] on zinc oxalate and also by the work of Wheeler and Galwey [6] on various nickel oxysalts. The use of gas adsorption studies utilising generally the physical adsorption of nitrogen at low temperatures [7] is another method whereby the changes in texture may be followed. Such textural changes may be altered by a change in the environment and this is demonstrated by changes in the surface area of manganese carbonate under different conditions of heat treatment [8].

Special techniques often impose special environments peculiar to the technique. This makes comparison between techniques difficult, for it must be remembered that the environment that ensures the best DTA signal is not the environment that will achieve the clearest and most accurate TG trace [9].

The effect of the environment can thus cause alterations in the course of the chemical reaction, the texture of the solid residue, and this in turn may be reflected either in the thermodynamic nature of the reaction, i.e. the position of the equilibrium state, or in the kinetics of the solid state decomposition. These points will now be discussed further.

Change in the course of decomposition

The influence of the environment in changing the course of a chemical reaction can be illustrated by reference to the decomposition of zinc oxalate and nickel oxalate [10, 11]. Ignoring the temperatures involved which vary from one TG unit or DTA unit to another, one has for zinc oxalate the following sequence of decomposition reactions;

$$ZnC_2O_4.2H_2O = ZnC_2O_4 + 2H_2O$$

DTA peak, endothermic in both N_2 and O_2.

$$ZnC_2O_4 = ZnO + CO + CO_2$$

DTA peak, endothermic in N_2.

In air or oxygen however:

$$CO + \tfrac{1}{2}O_2 = CO_2$$

This above reaction is catalysed by the zinc oxide product surface and is exothermic. The exothermic nature of the catalysed reaction produces an overall exothermic character to the DTA peak for the decomposition of zinc oxalate in air or oxygen. The more complicated DTA peaks observed sometimes for this part of the decomposition is due to the slow build up of solid zinc oxide which might not at first present enough surface to act as an effective catalyst, and in the latter part of the reaction the sintering of the zinc oxide can reduce its catalytic efficiency. This leads to the more complicated DTA signals received in certain circumstances for this type of decomposition (Figure 1).

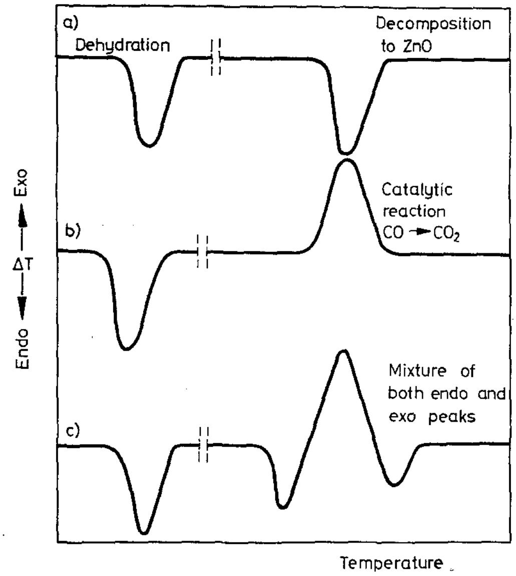

Fig. 1. DTA curves for zinc oxalate decomposition: (a) in nitrogen; (b) in oxygen or air; (c) in oxygen or air where DTA pattern is more complicated

In the case of the decomposition of nickel oxalate dihydrate a similar change from an endothermic decomposition peak in nitrogen to an exothermic peak in air or oxygen is observed but for a very different reason. The dehydration process is again endothermic in both nitrogen or oxygen;

$$NiC_2O_4.2H_2O = NiC_2O_4 + 2H_2O$$

DTA peak, endothermic in both N_2 and O_2.

The decomposition is to the metal;

$$NiC_2O_4 = Ni + 2CO_2$$

DTA peak, endothermic in N_2.

In air however the metal is oxidised;

$$Ni + \frac{1}{2}O_2 = NiO$$

This is a violently exothermic reaction especially at the temperature of decomposition. The pyrophoric nature of the metal is mainly due to its finely divided state giving it a surface area as determined by nitrogen adsorption of up to 150 m^2g^{-1} [12]. The overall reaction in air is thus exothermic. The more complicated DTA signals that can be found in some conditions arise because product nickel is initially present only in small quantities and towards the end of the reaction the heat generated causes the metal to sinter and so become less pyrophoric, thus allowing the basic endothermic peak to reappear. A further contributing factor to the more complicated DTA peaks sometimes seen for nickel oxalate decomposition in air is the shielding influence of the CO_2 product gas which does not allow the oxygen to react with the nickel metal until it is swept clear of the solid residue by the current of air or oxygen used in the DTA experiment. These points are all illustrated in Figure 2.

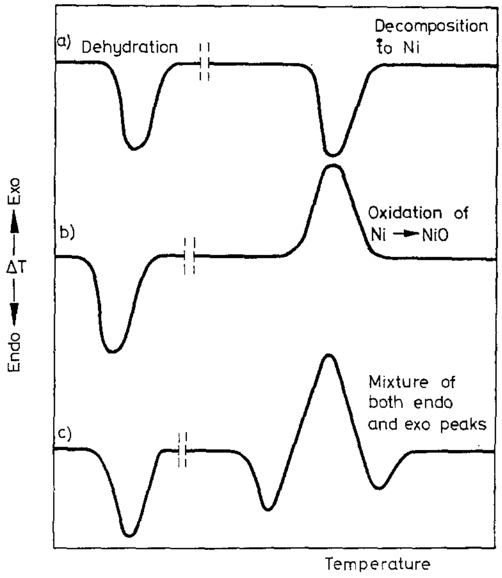

Fig. 2. DTA curves for nickel oxalate decomposition: (a) in nitrogen; (b) in oxygen or air; (c) in oxygen or air where DTA pattern is more complicated

It should be mentioned that under all conditions the dehydration of these salts is endothermic. Certain oxalates decompose to the carbonate and again the subsequent decomposition of the carbonate is endothermic under all environments. Thus calcium oxalate monohydrate has a decomposition sequence;

$$CaC_2O_4.H_2O = CaC_2O_4 + H_2O$$

DTA peak, endothermic

$CaC_2O_4 = CaCO_3 + CO$
DTA peak, endothermic in N_2 often exothermic in air or O_2

$CaCO_3 = CaO + CO_2$
DTA peak, endothermic

It was thought that the exothermic behaviour of the calcium oxalate in air must imply a catalytic effect on the reaction,

$$CO + \tfrac{1}{2}O_2 = CO_2$$

by the product calcium carbonate [10]. It now seems more likely however that the above reaction may be catalytically induced by parts of the DTA cell assembly.

In other variable valency oxalate decompositions the reaction in nitrogen leads to the production of the lowest valency oxide. Thus in the decomposition of manganese oxalate in nitrogen the oxide MnO is produced, whilst in the presence of oxygen higher valency oxides are produced, i.e. Mn_3O_4, Mn_2O_3 or MnO_2. The transformation temperatures for these oxides at one atmosphere of air have been given by Honda and Stone [13] as;

$$MnO_2 \xrightarrow{535^\circ} Mn_2O_3 \xrightarrow{933^\circ} Mn_3O_4 \xrightarrow{1160^\circ} MnO$$

The accuracy of these early observations may be in doubt especially that given for the $Mn_3O_4 \rightarrow MnO$ conversion however it seems that the oxide stable at the temperature of decomposition in air or oxygen is the product oxide ultimately formed in the thermal decomposition of manganese oxysalts [8]. It is possible that this might be the basis for a more general observation applicable to the thermal decomposition of all oxysalts producing oxides of variable valency.

Finally in this section it must be pointed out that certain oxysalts possess anion radicals whose oxidising capability ensures that the highest valency oxide is produced. This is true of nitrate decompositions where the product oxide is always in the highest valency form and the environmental gas has no influence on the course of the chemical reaction. However these nitrate decompositions may be complicated by other environmental factors.

Alteration in the physical nature of solid product

The environment can cause an alteration in the physical nature of the solid product and this can be followed in terms of the density [14], the surface area as determined by adsorption experiments [8], by optical microscopy or by electron microscopy [5]. The environmental factor here is the size and shape of the original reacting particles, the degree of compaction and adhesion between particles imposed on the sample, and whether the product gases are removed as quickly as possible under vacuum conditions or at atmospheric in a flow of carrier gas.

The theory behind the changes in particle size or surface area during the course of decomposition have been set out very clearly by Gregg [15] and quantitative correlations made between the kinetics of decomposition and the surface area in a general form by Nicholson [16] and in a special case by Dollimore and Tinsley [17] with reference in the latter instance to the decomposition of lithium oxalate. Briefly the increase in surface area or a decrease in particle size is caused by a shattering of the original particles. This is caused by strains set up due to differences in the densities of the solid reactant and product causing a distortion of the reaction interface.

The shape of the original particles largely determines the subsequent changing shape of the reaction interface in the course of the thermal decomposition. If the reaction rate per unit area of reaction interface is constant then a zero order reaction will result. The most obvious case is growth of reaction interface from the two large faces of a plate-like crystal [18, 19]. However a more usual effect of the shape of particles is seen in the kinetics for spherically shaped reaction interfaces contracting inwards, or the contracting area condition also observed in some cases [20]. To a certain extent the shape of the original crystallite and hence the contracting interface is influenced by the prehistory and the method of preparation of the sample. Thus samples of calcium carbonate have been prepared in our laboratory which show all forms of deceleratory kinetic laws reflecting different reaction interface kinetics. It is normally assumed that these reflect the behaviour of single particles multiplied by a factor which represents the total weight of the sample. However in powder compacts an additional factor is the spread of the reaction interface via the points of adhesion [20]. All these are changes in behaviour caused by the initial condition, which then produce an alteration in the texture of the solid product.

The gas above the sample during decomposition can also influence the texture. Thus magnesium hydroxide decomposition in vacuum produces a product oxide which has a surface area many times greater than the same product oxide produced by decomposition in nitrogen at one atmosphere. This observation applies to other oxysalt decompositions. Water vapour can have a drastic effect on the texture of the resultant material in solid state decompositions. Thus the dehydration process in vacuum or low water vapour pressure often produces an amorphous anhydrous material with a high surface area whilst at a higher vapour pressure of water a crystalline anhydrous product results with a much smaller surface area [21, 22]. The influence of water vapour in affecting both the nature of the nitrogen adsorption isotherm and the surface area of a solid is clearly demonstrated in sintering studies on zinc oxide [23].

The presence of impurities in the original oxysalt can cause upon thermal decomposition wide variations in surface area and porosity. This is especially true if the foreign cations are incorporated into the oxysalt structure by suitable doping procedures. Typical results for doped cadmium carbonate samples [24] are shown in Tables 1 and 2. The pattern of behaviour varies according to the "foreign" ion incorporated in the lattice. The Tables show the effect of doping with Al^{3+},

Table 1

Specific surface areas, percentage decomposition and relative surface area for pure and doped heat treated cadmium carbonate samples
[Ref. 24]

Sample	% Decomposition	Specific surface area, m^{2}g^{-1}	Relative surface area
A 110	—	6.4	1.00
200	2.83	7.3	1.14
300	14.69	7.6	1.14
400	98.80	6.4	0.95
500	100.00	3.2	0.50
600	100.00	2.6	0.41
B I 110	—	7.8	1.00
200	5.7	7.8	1.00
300	72.6	3.1	0.39
400	98.4	4.9	0.66
500	99.9	5.8	0.78
600	100.0	5.7	0.77
B II 110	—	5.9	1.00
200	8.5	5.9	1.00
300	80.7	5.2	0.88
400	99.8	6.6	1.12
500	99.9	6.0	1.02
600	100.0	5.2	0.88
B III 110	—	8.0	1.00
200	25.4	7.5	0.90
300	87.9	7.3	0.89
400	99.8	9.2	1.10
500	100.0	9.1	1.09
600	100.0	8.1	1.01
C I 110	—	8.3	1.00
200	4.79	8.4	1.01
300	67.44	14.5	1.74
400	99.10	10.5	1.27
500	100.00	6.3	0.76
600	100.00	4.2	0.51

Footnotes to Table 1

1. Symbols for samples
   - A. Undoped cadmium carbonate
   - B. Doped with Al^{3+}
   - C. Doped with Li^{+}

I indicates doping at 1 atom %
II indicates doping at 5 atom %
III indicates doping at 10 atom %
100, 110, 200 etc. refers to temperature of heat treatment at 10h in air

2. At temperatures of 500°, 600° results for % decomposition are corrected to account for oxygen loss from CdO lattice

Table 2

The variation of the mean pore radius and total pore volume for pure and doped cadmium carbonate samples as a function of temperature (Ref. 24)

Sample	Specific surface area, m^2g^{-1}	Total pore volume, V_p, ml · g^{-1}	Mean pore radius r_{mean}, Å
A 110	6.4	0.0324	59
200	7.3	0.0562	154
300	7.6	0.0306	83
400	6.1	0.0217	71
500	3.2	0.1025	641
600	2.6	0.1812	1394
B I 110	7.8	0.0844	216
200	7.8	0.0666	171
300	3.1	0.0236	152
400	4.9	0.0347	142
500	5.8	0.0398	137
600	5.7	0.0520	183
C I 110	8.3	0.2272	547
200	8.4	0.1773	482
300	14.5	0.2964	509
400	10.5	0.5742	1094
500	6.3	0.3417	1085
600	4.2	0.2249	1047

For explanation of symbols in first column see Table 1

and Li^+, other divalent ions, namely Zn^{2+}, Ca^{2+} and Ba^{2+} incorporated in the original lattice structure had no appreciable effect when compared to the heat treated undoped cadmium carbonate. It is not surprising that with these changes in texture the kinetics of decomposition are also affected [25].

The equilibrium condition

The basic laws of thermodynamics reveal that the equilibrium condition depends upon environmental factors especially of temperature and pressure [26]. The actual systems found in practice for solid state decompositions vary but all fit into the general equation;

$$xR_s \rightleftharpoons yP_s + zP_g$$

where R_s denotes a solid reactant, P_s a solid product and P_g a gaseous product and x, y and z are the numbers required to balance the equation.

Examples which may be cited to demonstrate this wide range are;

$$4MnO_{2(s)} = 2Mn_2O_{3(s)} + O_{2(g)}$$

$$6Mn_2O_{3(s)} = 4Mn_3O_{4(s)} + O_{2(g)}$$

$$CaCO_{3(s)} = CaO_{(s)} + CO_{2(g)}$$

and

$$CuSO_4.5H_2O_{(g)} = CuSO_4.3H_2O_{(s)} + 2H_2O_{(g)}$$

To conform to the general concept of thermodynamics the processes under consideration should be reversible. This is not always so experimentally yet a number of solid state decompositions which fall into this latter category do in fact obey the thermodynamic equations. There are however a further class of thermal solid state decompositions where the equilibrium condition is such that the "decomposition temperature" is invarient with respect to pressure.

The free energy of the system represented by the general equation with $x = I$ is;

$$G = n_{R_s}\mu_{R_s} + n_{P_s}\mu_{P_s} + n_{P_g}\mu_{P_g}$$

The subscripts refer to the materials mentioned above, n is the number of moles and μ is the chemical potential of the pure substances.

The solid reactant and product have chemical potentials which depend only on temperature. The chemical potential of the gaseous product however depends on both pressure and temperature, i.e.;

$$\mu_{P_g} = \mu^0_{P_g} + RT\ln P_g$$

where $\overset{\circ}{\mu}_{P_g}$ represents the chemical potential of the gaseous product at standard pressure.

If the free energy of the system is $(G + dG)$ when dn moles of R_s have decomposed, and using the condition $\frac{dG}{dn} = 0$ for the equilibrium condition then

$$y\mu_{P_s} + z\overset{\circ}{\mu}_{P_g} - \mu_{R_s} = -zRT\ln P_{P_g}$$

All the chemical potential terms in this equation are constant at a given temperature, so that at equilibrium;

$$P^z_{P_g} = K_P$$

or

$$P_{P_g} = \text{const.}$$

The value of P_{P_g} is the dissociation or equilibrium pressure at that temperature. The standard free energy change of the reaction, ΔG°, is the value of $\frac{dG}{dn}$ when the gaseous product is at a partial pressure of one atmosphere, i.e.

$$\Delta G^\circ = -RT \ln K_{P_g}$$
$$= -RT \ln P_{P_g}$$

(for the simple case where $z = 1$).

The variation of the equilibrium or dissociation pressure with temperature can be developed by conventional thermodynamic methods leading to;

$$\ln K_P = \frac{-\Delta H}{RT} + \text{const.}$$

or

$$\ln P_{P_g} = \frac{-\Delta H}{RT} + \text{const.}$$

The dependence of the the decomposition upon the environmental pressure of product gas is now obvious. Many systems conform to the expectations of the above equation even if not strictly irreversible in the thermodynamic sense. Thus if product gas is present in the experimental environment during decomposition of an oxysalt in the solid state then the decomposition temperature corresponds to the temperature obtained by substituting appropriate values of P_{P_g} and ΔG° in in the above equations. In DTA experiments in particular the variation of the peak temperature or initial temperature of the peak (i.e. the point of departure from the base line) with pressure can be used to construct plots of the temperature at the start of various peaks against the vapour pressure of the product gas and then the plots of logarithm of the pressure against the inverse of the decomposition temperature in degrees Kelvin. The use of DTA in this respect is more advantageous than the more conventional equipment as it allows much more complicated

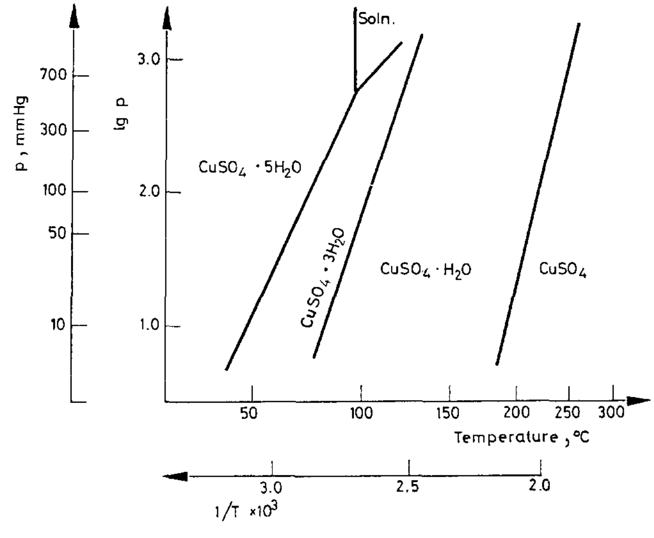

Fig. 3. The effect of water vapour on the dehydration of $CuSO_4.5\,H_2O$. (Berg et al., Ref. [29])

systems to be investigated. Such an approach has been applied to the dehydration of $Al_2(SO_4)_3.16H_2O \rightarrow Al_2(SO_4)_3.14H_2O \rightarrow Al_2(SO_4)_3.12H_2 \rightarrow Al_2(SO_4)_3.9H_2O \rightarrow$ $\rightarrow Al_2(SO_4)_3.6H_2O$, by Barret and Thiard [27], to oxide dissociations of manganese by Matsushima and Thoburn [28] and by Berg et al. [29] for the various dehydration steps in $CoSO_4.7H_2O$ and $CuSO_4.5H_2O$ (Figure 3).

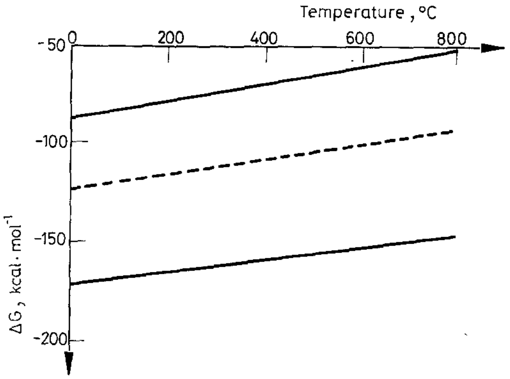

Fig. 4. The Ellingham free energy diagrams for the free energy of formation of various oxides (schematic representation) dotted line; $CO + 1/2\,O_2 = CO_2$; above dotted line; product is metal in oxalate decomposition; below dotted line; product is oxide in oxalate decomposition

The thermodynamic arguement can also be developed to deal with the equilibrium condition when more than one gas is present in the products. This has been set out by Dollimore et al. [11]. In this case use is made of the Ellingham free energy diagrams [30]. These show the variation of ΔG, the free energy of formation of various oxides with temperature and data in this form is schematically portrayed in Figure 4.

The equations for the two possible reactions for divalent oxalate decompositions are;

$$MC_2O_4 \rightleftharpoons MO + CO + CO_2$$

and

$$MC_2O_4 \rightleftharpoons M + 2CO_2$$

For the equilibrium condition for the first reaction, the equilibrium constant K_1 is given by;

$$K_1 = \frac{[MO][CO][CO_2]}{[MC_2O_4]}$$

and for the second reaction the equilibrium constant K_2 is given by;

$$K_2 = \frac{[M][CO_2]^2}{[MC_2O_4]}$$

The ratio K_1/K_2 is then given by:

$$\frac{K_1}{K_2} = \frac{[\mathrm{MO}][\mathrm{CO}]}{[\mathrm{M}][\mathrm{CO_2}]}$$

In all these equations the use of square brackets denote activities.
A similar ratio can be obtained by considering the reactions;

$$2\mathrm{CO} + \mathrm{O_2} = 2\mathrm{CO_2}$$

$$2\mathrm{M} + \mathrm{O_2} = 2\mathrm{MO}$$

Letting K_3 denote the equilibrium constant for the $\mathrm{CO} \rightarrow \mathrm{CO_2}$ reaction and K_4 that for the oxidation of the metal gives;

$$\left(\frac{K_4}{K_3}\right)^{1/2} = \frac{[\mathrm{MO}][\mathrm{CO}]}{[\mathrm{M}][\mathrm{CO_2}]}$$

Then;

$$\frac{K_1}{K_2} = \left(\frac{K_4}{K_3}\right)^{1/2}$$

If the standard free energy of formation, $\Delta G^\circ = -RT \ln K$, for $\mathrm{CO} \rightarrow \mathrm{CO_2}$ is given by ΔG_a, and for the oxide formation by ΔG_b, then for $\Delta G_a > \Delta G_b$,t hen $K_3 < K_4$ and it follows that $K_1 > K_2$. This can be interpreted as meaning that the oxalate solid state decomposition to the oxide predominates over the decomposition to the metal. In the usual experiment where the product gas is removed as formed in the inert carrier gas this means that the reaction proceeds to the oxide. If however $\Delta G_b > \Delta G_a$ then in the usual experiment the reaction will proceed to the metal. Similar arguements can be set out for oxalates of trivalent metals. With reference to the Ellingham free energy diagrams the above arguements simply mean that if the free energy line for the formation of a metal oxide lies above that for the free energy of formation of carbon dioxide from carbon monoxide then the metal is the end product of oxalate decomposition. If however the free energy line for the formation of the metal oxide lies below that for the free energy of formation of carbon dioxide from carbon monoxide then the metal oxide is the end product of oxalate decomposition.

The environmental factor in kinetic determinations

The classical method of obtaining kinetic data for solid state thermal decompositions is to determine the form of the kinetic expression from isothermal experiments at various temperatures and to show that the experiments at different temperatures are isokinetic. The variation of the specific reaction rate with temperature is then shown by assigning values for the pre-exponential term and the activation energy in the Arrhenius equation. However the kinetic data thus collected shows a marked dependence upon environmental factors.

If the weight of sample, used, or the form of packing the sample offers a barrier to the loss of product gas then the kinetic laws may be shown to be those due to diffusion. Alternatively the diffusion process may be that of ionic species moving to the reaction interface. In any case the kinetics shows an environmental dependence upon the above factors which can easily be demonstrated experimentally. A similar marked environmental effect is shown experimentally for the thermal decomposition of samples identical except for their particle size. All these effects on the kinetics of decomposition arise because the reaction in solid state decompositions is located at a reaction interface and is initiated by a process of nucleation. These two points and the consequent environmental nature of the subsequent kinetic laws which arise out of these circumstances have recently been discussed in detail elsewhere [31]. The main difficulty is the recognition of these laws which are largely based on the geometry of an increasing or decreasing reaction interface plus in some circumstances a dependence upon diffusion processes to or from the interface [32, 33].

However a recognition of all these environmental aspects of the kinetics of solid state decomposition still leaves one important aspect to be discussed, namely the pressure of the environmental gas. One would normally expect in accordance with Le Chateliers principle that an increase in pressure of the product gas over the sample would cause a decrease in the rate of reaction with an apparent increase in the activation energy. In many of the investigations under study this is in fact the experimental observation. This is due to an increase in the back reaction and under such conditions the equation describing such a decomposition should be written;

$$A_{(s)} \rightarrow B_{(s)} + C_{(g)}$$

tho show recognition of this fact. The solid residue should always be examined to see if the reaction has proceeded to completion or if the product is a mixture as indicated by the above equation. Due to the nature of the reaction interface and the lack of thermodynamic reversibility shown by some systems this point should always be established by experimental observation.

There is however one product gas which often causes anomalous kinetic behaviour. This is water vapour and it givves rise to the Smith–Topley effect [34, 35] It was shown by these two authors in studies on the dehydration of manganous oxalate dihydrate and cupric sulphate pentahydrate that at low pressures of water vapour the dehydration rate constant decreased with increasing water vapour pressure until a critical pressure was reached. The rate constant then increased sharply and in the higher pressure region the behaviour in the presence of water vapour was normal. The initial behabiour upon dehydration at low relative vapour pressure of water vapour has been shown to be associated with the production of an amorphous dehydrated product whilst in the second region at higher water vapour pressure the dehydrated product was crystalline. One thus has both the system;

$$MXxH_2O_{(s)} = MX_{\text{amorphous}} + xH_2O_{(v)}$$

and

$$MXxH_2O_{(s)} = MX_{crystalline} + xH_2O_{(v)}$$

behaving normally with respect to water vapour pressure ($MXxH_2O_{(s)}$ represents a solid hydrated salt, $MX_{amorphous}$ the amorphous dehydrated product, $MX_{crystalline}$ the crystalline dehydrated product and $xH_2O_{(v)}$ the water lost in the reaction). The abnormal behaviour is simply the appearance of the amorphous product under vacuum or low water vapour conditions and the appearance of a crystalline product in the higher vapour pressure region. It would also seem necessary to explain why the effect is not widely reported for other vapours or gases.

A very simple explanation of the effect is to first point out that the strain caused at the reaction interface during decomposition is often sufficient to cause complete disruption of the solid residue with an increase in surface area so that the product appears amorphous to X-ray diffraction techniques [15]. However above a certain low critical vapour pressure water vapour has a profound effect upon ionic mobility either through the surface or through the bulk of the solid. This is a well known phenomenon in sintering [23]. The effect is to cause a recrystallisation process to occur or a growth in particle size so that the material becomes crystalline to X-ray diffraction studies. We thus have beyond a given vapour pressure of water a crystalline anhydrous product appearing in contrast to the amorphous anhydrous product appearing in the vacuum or low water vapour region. This kind of explanation explains many of the studies on the Smith–Topley effect recently reported [21, 22] but Watelle-Marion et al. [36] have put forward alternative explanations based upon the appearance of a meta-stable phase established when the temperature and pressure imposed upon the initial system are far away from its condition of equilibrium. If the metastable phase is considered to appear because of the strain set upon the system particularly at the reaction interface then the two explanations have a common basis.

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Résumé — L'environment peut influer sur la décomposition thermique d'un oxysel en provoquant: a) un changement pendant la décomposition thermique, b) une altération de la nature physique du produit solide ou des phases intermédiaires solides.

L'environment peut aussi exercer un effet sur les conditions d'équilibre ou sur la cinétique. L'emploi de techniques spéciales, comme la thermogravimétrie, l'analyse thermique différentielle ou l'analyses calorimétrique différentielle (DSC), pour étudier la décomposition, signifie qu'un environnement particulier est imposé à l'oxysel et qu'il exerce un effet sur le processus de la décomposition thermique.

L'influence de l'environnement sur le déroulement d'une réaction chimique peut être illustré à l'aide des décompositions de l'oxalate de zinc et de l'oxalate de nickel. L'ATD montre que les décompositions sont endothermiques en atmosphères inertes mais exothermiques dans l'air ou l'oxygène. Les causes en sont pourtant différentes dans les deux cas. Ainsi, bien que le produit de la déomposition de l'oxalate de zinc soit l'oxyde de zinc, le changement de sens de l'effet thermique (endothermique → exothermique) est dû à l'oxydation catalytique de l'oxyde de carbone en dioxyde de carbone, en présence d'oxygène. Le changement similaire du sens de l'effet thermique dans le cas de l'oxalate de nickel est dû à la formation de nickel en atmosphère inerte et à celle d'oxyde de nickel dans l'air ou dans l'oxygène.

L'altération de la nature physique des produits solides peut être illustrée par des mesures de surface, effectuées sur les résidus solides de décomposition des carbonates ou des oxalates. Les études cinétiques et d'équilibre chimique montrant l'influence de l'environnement, sont illustrées par les phénomènes de déshydratation et de décomposition de carbonates et d'oxalates.

Zusammenfassung — Die Umgebung kann die thermische Zersetzung eines Oxysalzes auf folgende Weise beeinflussen: a) durch Verursachen einer Änderung im Verlauf der chemischen Zersetzung
oder, b) durch Verursachen einer Veränderung in der physikalischen Beschaffenheit des festen Produktes oder der festen Zwischenprodukte.

Die Umgebung kann sich auch auf den Gleichgewichtszustand oder den Verlauf der Kinetik auswirken. Der Einsatz spezieller Techniken, wie Thermogravimetrie, Differentialthermoanalyse oder Differentialabtastkalorimetrie zum Studium der Zersetzung bedeutet, daß dem Oxysalz eine spezielle Umgebung aufgezwungen wird, wodurch der thermische Zersetzungsprozess beeinflusst wird.

Die Wirkung der Umgebung in der Änderung des Verlaufs einer chemischen Reaktion kann an Hand Zersetzung von Zink-oxalat und Nickel-oxalat veranschaulicht werden. Die DTA-Kurve zeigt, daß die Zersetzungen in inerten Atmosphären endotherm, in Luft oder Sauerstoff hingegen exorherm verlaufen. Die Ursache hierfür ist jedoch in den zwei Fällen verschieden. Obwohl das Zersetzungsprodukt von Zink-oxalat jeweils Zinkoxid ist, ist die Änderung des Charakters der Zersetzung vom endothermen zum exothermen eine Folge der katalytischen Oxidation von Kohlenmonoxid zu Kohlendioxid in Gegenwart von Sauerstoff. Eine ähnliche Änderung im Charakter der Zersetzung von Nickel-oxalat kann der Bildung von Nickel in einer inerten Atmosphäre und der von Nickeloxid in Luft oder Sauerstoff zugeschrieben werden.

Die Änderung in der physikalischen Bechaffenheit der festen Produkte wird an Hand von Oberflächenmessungen an festen Rückständen der Zersetzung von Carbonaten oder Oxalaten veranchaulicht. Untersuchungen der Kinetik und der chemischen Gleichgewichte, welche den Einfluss der Umgebung zeigen, werden an Hand der Dehydratierungsstudien, sowie der Zersetzungen von Carbonat und Oxalat veranschaulicht.

Резюме — Окружающая среда может оказывать следующие влияния на термическое разложение каких-либо оксисолей: а) вызывая изменение в ходе химического разложения или б) вызывая перестройку физической природы твердого продукта или же твердых промежуточных продуктов. Окружающая среда может также затрагивать равновесные условия или порядок кинетики. Использование такой специальной техники как термогравиметрия, дифференциальный термический анализ или дифференциальная сканирующая калориметрия для изучения разложения, означает, что специальная окружающая среда налагается на разложение оксисоли и на эффекты процесса термического разложения. Влияние окружающей среды на изменение хода химической реакции может быть показано на примере разложения оксалатов цинка и никеля. ДТА показывает, что разложение их в инертной атмосфере —эндотермическое, но в атмосфере воздуха или кислорода — экзотермическое. Однако, в каждом случае причины этого явления разные. Так, хотя продуктом разложения оксалата цинка является окись цинка, изменение характера разложения от эндотермического до экзотермического, обусловлено каталитическим окислением окиси углерода до двуокиси в присутствии кислорода. Подобные изменения характера разложения оксалата никеля, однако, обусловлены образованием никеля в инертной атмосфере, но окиси никеля в атмосфере воздуха или кислорода. Изменение физической природы твердых продуктов проиллюстрировано изменениями поверхностной площади на твердых остатках разложения карбонатов о оксалатов. Влияние окружающей среды на кинетические и химические равновесия проиллюстрировано на примере изучения дегидратации продуктов и оксалатов.