

Table 1. SURFACE HYDROXYL FREQUENCIES ON ANATASE PIGMENTS

Description	Al <sub>2</sub> O <sub>3</sub> (%)	SiO <sub>2</sub> (%)	$\gamma$ OH (cm <sup>-1</sup> )
No treatment*	<0.025	0.30	3,685
Simple treatment*	0.39	0.56	3,687
Complex treatment*	2.04	0.97	3,683, 3,725 sh

\* 'Treatment' refers to the manufacturing technique of modifying TiO<sub>2</sub> surfaces with, for example, alumina and silica (ref. 4, 276). Commercial pigments also contain other trace components.

The observation of more than one surface hydroxyl band on some oxides<sup>1,2</sup> may similarly be explained. Thus Yates has suggested that two bands for anatase may be due to hydroxyl groups on different crystal faces<sup>1</sup>.

Each pigment grade showed similar behaviour towards *n*-octadecanoic acid, a *cis*-9-*cis*-12-octadecadienoic acid concentrate and *n*-octadecyl hydrogen phthalate (OHP). In the spectra of adsorbed OHP, the ester C=O stretching band of surface ions was found between 1,707 and 1,715 cm<sup>-1</sup> (cf. 1,720 cm<sup>-1</sup> for solid potassium salt of OHP), the corresponding band for adsorbed acid occurred near 1,725 cm<sup>-1</sup> (cf. 1,738 cm<sup>-1</sup> CCl<sub>4</sub> soln., 1,728 cm<sup>-1</sup> solid, for OHP), showing that for both surface ion and adsorbed acid the ester group is perturbed by the pigment surface. The spectra of adsorbed OHP showed normal intensity properties. However, the surface carboxylate ion had a marked enhancement of intensity of the aromatic in plane skeletal bands (about 1,450, 1,490, 1,580 and 1,600 cm<sup>-1</sup>). This may be due to their proximity to broadened bands of the —CO<sub>2</sub><sup>-</sup>, or—perhaps—to the aromatic ring lying flat on the pigment surface.

The spectra of *n*-octadecanol on all pigments examined were virtually identical, and closely resembled the spectrum of the fatty alcohol in solution. However, neither the unassociated hydroxyl band (3,640 cm<sup>-1</sup>) nor the surface hydroxyl band of the pigments was observed. Therefore, the alcohol is hydrogen bonded to the pigment surface.

This work is being supported by the U.S. Department of Agriculture under project number UR-E29-(40)-29. I thank Dr. L. A. O'Neill for his help during this work, and Prof. F. C. Tompkins for useful discussions.

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<sup>1</sup> Yates, D. J. C., *J. Phys. Chem.*, **65**, 746 (1961).

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<sup>4</sup> Barksdale, J., *Titanium, its Occurrence, Chemistry and Technology*, 325 (Ronald Press, New York, 1949).

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## Kinetic Parameters from Thermogravimetric Data

THE use of thermogravimetric data to evaluate kinetic parameters of solid-state reactions involving weight loss (or gain) has been investigated by a number of workers<sup>1-4</sup>. Freeman and Carroll<sup>2</sup> have stated some of the advantages of this method over conventional isothermal studies. To these reasons may be added the advantage of using one single sample for investigation. However, the importance of procedural details, such as crucible geometry, heating rate, pre-history of sample, and particle size, on the parameters has yet to be fully investigated. It is also necessary to ensure accurate temperature measurement, both for precision and also to detect any departure from a linear heating rate due to endo- or exo-thermic reactions. (The effect of these may be largely eliminated by the use of small samples.) In our present work (using a Stanton HT-D thermobalance) the sample temperature is measured directly by means of a thermocouple the bead of which is positioned in or near the sample, depending on crucible design, the wires of which run down a twin-bore rise rod. The connexion between the end of the thermocouple wires

on the balance arm and the terminal block is made by 0.001 in. platinum and platinum/rhodium wires<sup>5</sup>. It has been shown that these wires do not affect the performance of the balance but act merely as a subsidiary damping. From the terminal block compensated cable leads to the cold junction and a potentiometric arrangement for direct measurement of the thermocouple output.

*A priori* knowledge of the value of the order of reaction is assumed in most derivations<sup>1,3,4</sup>, while the method<sup>2</sup> which allows for the determination of both the activation energy and the order of reaction suffers from a number of disadvantages<sup>6,7</sup>.

In the reaction  $aA_{(s)} \rightarrow bB_{(s)} + cC_{(g)}$ , the rate of disappearance of *A* may be expressed by:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (1)$$

where  $\alpha$  = fraction of *A* decomposed at time *t*, *n* = order of reaction, and *k* = rate constant given by the expression:

$$k = Ae^{-E/RT} \quad (2)$$

where *A* = frequency factor, and *E* = activation energy of the reaction.

For a linear heating rate of, say, *a* deg. min<sup>-1</sup>:

$$a = dT/dt \quad (3)$$

Combining equations (1), (2), and (3), rearranging and integrating: we get:

$$\int_0^a \frac{d\alpha}{(1 - \alpha)^n} = \frac{A}{a} \int_0^T e^{-E/RT} dT \quad (4)$$

The right-hand side of equation (4) has no exact integral, but by making the substitution  $u = E/RT$  and using the relation:

$$\int_u^\infty e^{-u} u^{-b} du \simeq u^{1-b} e^{-u} \sum_{n=0}^{\infty} \frac{(-1)^n (b)_n}{u^{n+1}} \quad (\text{see ref. 8})$$

equation (4) becomes:

$$\frac{1 - (1 - \alpha)^{1-n}}{1 - n} = \frac{ART^2}{aE} \left[ 1 - \frac{2RT}{E} \right] e^{-E/RT} \quad (5)$$

taking logs:

$$\log_{10} \left\{ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)} \right\} = \log_{10} \frac{AR}{aE} \left[ 1 - \frac{2RT}{E} \right] - \frac{E}{2.3RT} \quad (6)$$

for all values of *n* except *n* = 1 in which case equation (4), after taking logs:

$$\log_{10} \left[ -\log_{10} \frac{(1 - \alpha)}{T^2} \right] = \log_{10} \frac{AR}{aE} \left[ 1 - \frac{2RT}{E} \right] - \frac{E}{2.3RT} \quad (7)$$

Thus a plot of either  $\log_{10} \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)} \right]$  against  $\frac{1}{T}$

or, where *n* = 1,  $\log_{10} \left[ \frac{-\log_{10}(1 - \alpha)}{T^2} \right]$  against  $\frac{1}{T}$

should result in a straight line of slope  $-E/2.3R$  for the correct value of *n*, since it may be shown that for most values of *E* and for the temperature range over which

reactions generally occur the expression  $\log_{10} \frac{AR}{aE} \left[ 1 - \frac{2RT}{E} \right]$

is sensibly constant.

The equations may be applied by a simple graphical technique. Since there is theoretical justification for orders of reaction of 0, 1/2, 2/3, and 1 in solid-state

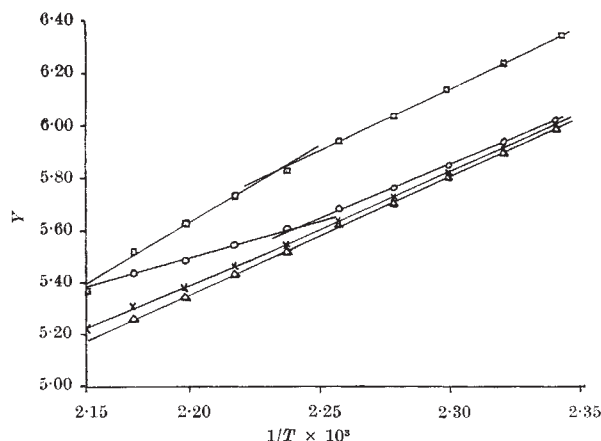


Fig. 1. Water loss from calcium oxalate monohydrate

$$Y = -\log \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^n (1 - n)} \right] \text{ for } n = 0, 1/2 \text{ and } 2/3$$

$$\text{and } -\log \left[ \frac{-\log (1 - \alpha)}{T^n} \right] \text{ for } n = 1$$

$$\Delta, n = 2/3; \times, n = 1/2; \circ, n = 0; \square, n = 1$$

kinetics<sup>9</sup> it is possible to substitute these values into equation (6) (or equation 7 when  $n = 1$ ) to obtain the appropriate plots. This is illustrated in Fig. 1 for the water loss from calcium oxalate monohydrate, from which it is seen that the results best fit a 2/3 order and the calculated activation energy becomes 21.7 kcal/mole which is in close agreement with much published work (as listed, for example, in ref. 2). It is also possible to use a computational approach to select a value of  $n$  which gives the best straight line through the points—on the assumption that the order is constant throughout the reaction.

Reaction	Table 1			
	Range of $\alpha$ studied	Heating rate deg. min <sup>-1</sup>	$E$ kcal/mole	$n$
$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 + \text{H}_2\text{O}$	0.17–0.77	3.45	21.4	0.71
$\text{CaC}_2\text{O}_4 \rightarrow \text{CaCO}_3 + \text{CO}$	0.12–0.71	3.14	62.0	0.38
$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	0.15–0.78	2.99	51.7	0.46

The reactions were carried out using 0.1 g starting material with either 1- or 2-g platinum crucibles in an air atmosphere.

The results in Table 1 have been derived in this way. Work is continuing, particularly with the view of examining the possible variation of  $n$  as the reaction proceeds.

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<sup>7</sup> Lukaszewski, G. M., and Redfern, J. P., *J. Chem. Soc.*, 4802 (1962).

<sup>8</sup> Rainville, E. D., *Special Functions*, 44 (Macmillan, 1960).

<sup>9</sup> See, for example, Garner, W. E. (ed.), *Chemistry of the Solid State* (Butterworth, 1955).

### Preparation of Ion-molecules of the Inert Gases in an Electromagnetic Isotope Separator

A RESURGENCE of interest in the chemistry of the inert gases has been stimulated by the recent discovery of well-defined compounds of xenon with oxygen<sup>1</sup> and fluorine<sup>2</sup>. Ion molecules of the inert gases of the types  $\text{KrH}^+$  (ref. 3),  $\text{KrI}^+$  (ref. 4),  $\text{KrCH}^+$  (ref. 5), etc., have also been produced

and identified in the mass spectrometer. Since the singly charged ions of the inert gases are isoelectronic with the halogens it is possible that a series of compound ions might be formed with alkali metals corresponding to the alkali halide salts.

In a preliminary attempt to confirm this hypothesis using the Atomic Energy Research Establishment's experimental electromagnetic isotope separator, well-defined beams of the ion molecules lithium argide,  $\text{LiAr}^+$  (Fig. 1), lithium kryptide,  $\text{LiKr}^+$  (Fig. 2), and rubidium argide,  $\text{RbAr}^+$ , have been characterized.

The isotope separator<sup>6</sup> is particularly well suited to this type of investigation since it has a resolving power comparable with that of mass spectrometers and an ion-source designed for routine high-temperature evaporation and ionization of metals and salts. The ions and molecules can interact in the field-free region of the ion-source plasma.

The ion beams were produced by running the discharge of the ion source<sup>6</sup> on a mixture of the inert gas and the vapour of the alkali iodide. At a total extracted ion beam intensity of several milliamperes (mainly  $\text{Li}^+$  and  $\text{I}^+$ )  $\mu\text{amp}$  beams of the compound ions were produced. In a similar experiment using a mixture of both lithium and lithium iodide, no significant increase in compound ion

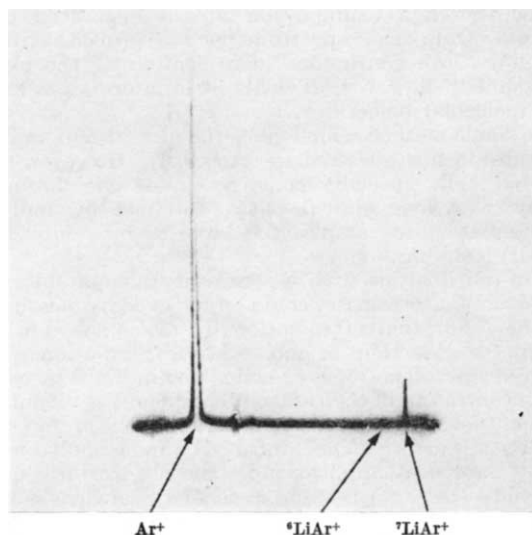


Fig. 1

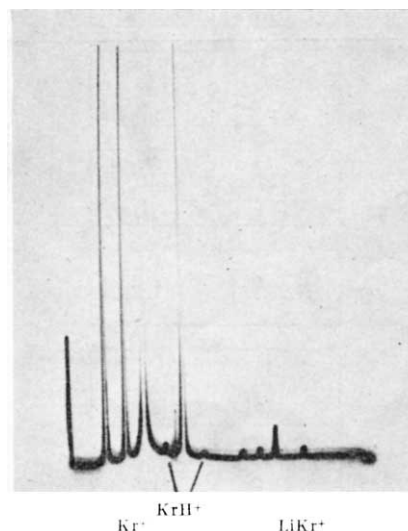


Fig. 2