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INTERNATIONAL SYMPOSIUM
ON
REACTION MECHANISMS OF INORGANIC SOLIDS

by

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INTERNATIONAL SYMPOSIUM
ON
REACTION MECHANISMS OF INORGANIC SOLIDS

The symposium was arranged by the Chemical Society and held at the University of Aberdeen during the week of 11-15 July 1966. Well over 200 scientists attended the week-long sessions. The French delegation was very much in evidence for a change, and distinguished by being the only group for which interpreters were provided. The conference banquet fell on Thursday evening, the 14th of July, Bastille Day. A fair majority of the French delegation was very late to the Friday session.

Not surprisingly, the papers at the conference fell into one of two categories; (1) crystallographers describing topotaxy in terms of inorganic reactions, and (2) chemists describing chemical reactions deduced from a variety of physical measurements and a bit of chemical analysis. Since the proceedings are not to be published, it is felt that the abstracts and/or titles will be of sufficient value to solid state chemists in the USA to warrant incorporation in report form.

PROGRAM

Monday, 11 July

a.m. Formalities-
Introductory address by Prof. J. A. Hedvall, Chalmers Tekniska Högskola, Gothenburg, Sweden.
Title: "The start and development of solid state chemistry".

p.m. Session on crystallographic studies of oxide, halide, nitrate, and silicate reactions.

1. "Topotaxy: A crystallographic approach to reactions of solids", by H.F.W. Taylor, Chemistry Department, University of Aberdeen.

2. "A study of topotaxy by oriented-crystal interaction of β-Ga_2O_3 and MgO", by G. Katz and R. Roy, Materials Research Laboratory, Penn. State Univ.

3. "Processes of leaching anhydrous layer silicates", by F. Liebau, Mineralogisch-Petrographisches Institut und Museum der Universität Kiel, W. Germany.

4. "Habit planes in binary alkali-halide systems", by P. Truelove and A. Hellawell, Oxford Univ.

5. "The interpretation of certain metastable structural states in crystalline solids in terms of the concept of antisymmetry", by J.D.C. McConnell, Cambridge Univ.

6. "Misfit and mechanism in structure changes of univalent nitrate and ammonium halide crystals", by S.W. Kennedy, University of Adelaide.

Measurements have been made to assess how far mechanism of transformation depends on misfit of the structures. The investigation follows the observation that reconstructive, martensitic, apparently coherent, and gradual transformations all occur between structurally similar phases in $TlNO_3$, and the third of these in its isomorphs also. Changes in lattice spacing have been measured, sometimes in coexisting phases, in single crystals of $TlNO_3$, $RbNO_3$ and $CsNO_3$. Measurements of mosaic spread were used to show what strains resulted. Super-coolings possible in nucleation and in growth were measured and are compared with meanings of the term "hysteresis". The reconstructive and martensitic transformations orthorhombic trigonal in $TlNO_3$ are alternatives. In the martensitic transformation the plane of minimum misfit (distortion) is not the habit (interfacial) plane but one perpendicular to it, (407). On this plane the misregister is 1.5% in one direction only. There is little evidence that the orientation of a habit plane must be rigorously reproducible, and there is some suggestion that it is not. At the transformation cubic to trigonal pseudo-cubic in all three substances growth seems to be as fast as heat transfer but there is an interface. Measurements on the coexisting phases show that there is a discontinuous change in lattice spacing in two directions of typically 0.6% in one plane with zero change in the perpendicular direction. Nucleation is much slower than propagation, super-coolings of 17°C have been attained. Strains, shown by a large increase in mosaic spread, are caused in the new phase. The crystals can be gradually annealed with the formation of sub-grains. This amount of two-dimentional misfit, combined with the values of elastic constants involved, is enough to cause measurable strains and to reduce nucleation rate but not enough to reduce growth rate appreciably or cause a semi-coherent martensitic type of interface which does occur in the transformation orthorhombic trigonal with a little over twice the misfit.

The orthorhombic structure transforms to the cubic in an apparently gradual manner with a diffuse interfacial region. Yet the least distorted plane still suffers a contraction along one direction of 1.6%. (This result depends on extrapolation of expansion coefficients which were measured for the purpose.) This suggests that the change in mechanism is largely due to greater thermal motion and reduced elastic constants.

In ammonium halides or the CsCl type NaCl type transformation the possibility of retaining a single crystal is greater, for a given crystal size, in the iodide, which is the softest. X-ray studies using image intensification indicate that a definite orientation relation is maintained.

7. "Vlasovite: a triclinic to monoclinic phase change", by J.R. Cann and S.G. Fleet, Cambridge University.

Vlasovite, a mineral of composition $Na_2ZrSi_4O_{11}$ previously reported as monoclinic by Pyatenko and Voronkov from an occurrence in the Kola Peninsula, Russia, has been found in rocks from Ascension Island in a triclinic twinned modification. The triclinicity is very slight (α and γ differ from 90° by less than 1°), and X-ray photographs show arrays of paired spots corresponding to diffraction by different parts of the crystal related by the twinning operation (reflection across (010)).

This vlasovite can be made to transform to the monoclinic variety by increasing the temperature. The inversion has been followed on a heating camera by observing the separation of the (100) and ($\bar{1}00$), and the (001) and ($00\bar{1}$) spots which give a measure of the triclinicity at different temperatures. The spots begin to move together at 15 - 18°C, and continue closing until they have completely coalesced at 29°C, when the crystals are monoclinic.

The triclinicity in this range is characteristic of the particular temperature and is not affected by thermal history; while the rate at which the characteristic triclinicity is adopted is so fast that no blurring of the spots on the five-minute exposure Laue photographs is observable. The transformation appears to be a displacive one similar to $\alpha \rightarrow \beta$ tridymite and $\alpha \rightarrow \beta$ cristobalite.

8. "The thermal dehydration of nekoite, $3CaO \cdot 6SiO_2 \cdot 8H_2O$", by Alastair W. Nicol, Dept. of Minerals Engineering, University of Birmingham, England.

A new analysis of the calcium silicate hydrate mineral nekoite has shown that the composition is $3CaO \cdot 6SiO_2 \cdot 8H_2O$. A thermal weight-loss curve has been determined by a quasistatic method and indicates that the water is lost in four principal stages, at 120°, 200°, 360-400° and 450°C, two water molecules being lost at each step. Loss of the first pair of water molecules commences at 40°C and is reversible up to 120°C when these are lost completely and reversible loss of the second pair begins and continues up to 200°C. Above 200°C reversible loss of the fifth water molecule occurs up to 250°C, when the irreversible loss of the sixth molecule commences, and the loss of this pair becomes complete by 400°C. At 450°C the last pair of water molecules is lost rapidly and irreversibly.

Parallel studies using single crystals show that all stages of the dehydration proceed topotaxially and applications of X-ray methods have permitted full descriptions of the phases formed and of their orientations relative to the original nekoite to be made. The phases formed at 120°C and 200°C, corresponding to the compositions $3CaO \cdot 6SiO_2 \cdot 6H_2O$ and $3CaO \cdot 6SiO_2 \cdot 4H_2O$ respectively, give quite sharp single crystal reflexions with little or no streaking; their diffraction patterns are very similar to that of nekoite and their unit cells correspond closely to the nekoite cell contracted along the c-direction. No separate phase is formed corresponding to the composition $3CaO \cdot 6SiO_2 \cdot 3H_2O$, and the X-ray pattern from the phase formed at 400°C, at an overall composition $3CaO \cdot 6SiO_2 \cdot 2H_2O$, shows marked streaking along powder directions in reciprocal space, suggesting a more drastic mode of formation for this phase compared with the two previous phases. The anhydrous phase formed at 450°C gives a correspondingly streaked pattern identical with that of xonotlite, $6CaO \cdot 6SiO_2 \cdot H_2O$, and it is thought that the structure of this phase must be closely similar to that of the natural mineral, possibly with one O^{-2} ion substituting for two OH^- ions. Finally, wollastonite is formed at 700°C in the same orientation to the last phase as Dent and Taylor (1956) found in the case of natural xonotlite.

Tuesday, 12 July

a.m. Session on Thermal and Other Reactions of Silicates and Layer Oxides.

1. "Kinetics and mechanisms of some mineral dehydroxylation reactions", by G.W. Brindley, Mineral Sciences Bldg., Penn. State Univ.

2. "The inhomogeneous mechanism of state change in dehydration reactions: the dehydration of norstrandite", by J.D.C. McConnell, Dept. of Mineralogy & Petrology, Cambridge Univ.

Norstrandite ($Al_2O_3 \cdot 3H_2O$) dehydrates at approximately 200°C producing a defect spinel structure with diffraction effects closely comparable to those given by bayerite when heated at the same temperature in air. Direct observation of the dehydration reaction for norstrandite in the electron microscope shows that during dehydration at 200°C a system of very fine cylindrical pores develops with the axes of the pores normal to the original sheet structure of the hydroxide. Heating at 400°C does not change the character of the fine pore structure.

In the interpretation of the corresponding dehydration reaction in the closely related compound bayerite, Lippens and de Boer suggested that a system of fine pores developed parallel to the sheet structure of the hydroxide. The present observations suggest that this is unlikely to be the case.

The general picture of the reaction mechanism for the dehydration of norstrandite which emerges from the present study is entirely compatible with the inhomogeneous reaction mechanism proposed originally by Ball and Taylor. It is thought also that the anisotropy of the diffusion of aluminium ions in the structure may play a large part in defining the actual mechanism and ultimate microstructure of the reaction product.

3. "Dehydration of goethite in an inert atmosphere", by J. Lima-de-Faria, Laboratório TFQMP da Junta Investigações do Ultramar, Lisboa, Portugal.

Single crystal X-ray studies of the dehydration of goethite in an inert atmosphere (N_2) at relatively low temperatures (350°-500°C) show that hematite and magnetite are both formed topotactically.

4. "Interparticle bonding by reactive hot pressing", by A.C.D. Chaklader, Dept. of Metallurgy, Univ. of British Columbia.

Attempts have been made to achieve interparticle bonding in solids by applying a pressure on a powder compact, while the material is undergoing a phase transformation. In a broader sense, this phase transformation may be either a polymorphic transition, a decomposition or a dissociation reaction. The application of pressure during a phase transformation is termed reactive hot pressing. Essentially, this process utilizes the high reactivity of solid during a phase transformation to achieve interparticle bonding. Enhanced reactivity of solids during a phase transformation is well known due to the work of J.A. Hedvall, and this is known as the "Hedvall effect".

Several sets of experiments were carried out with different kaolinitic clays, hydroxides of alumina, several carbonates and coals. Experiments with kaolinitic clay showed that strength and bulk density of the compacts are linearly related to the applied pressure during the dehydroxylation reaction and approximately proportional to the amount of dehydroxylation produced in the clay compacts. At a particular temperature and under a fixed pressure, the strength and density attained a constant value as soon as the dehydroxylation reaction reached a pseudo-equilibrium state.

5. "Some crystallographic studies of the effects of oxidation upon olivines", by P.E. Champness and P. Gay, Dept. of Mineralogy & Petrology, Cambridge Univ.

Data have been obtained using single crystals of selected olivines subjected to atmospheric oxidation at different temperatures and for different periods of time. All specimens have been examined by single crystal X-ray methods, supplemented in some cases by optical and electron microscopy.

It is confirmed that the initial effect of oxidation is the exsolution of iron oxides (ahematite-like phase and spinel-like phase) and that these are oriented with respect to the host olivine crystal. For both these phases the twinned orientations are those expected if structural control of the exsolution is exercised by the approximately close-packed oxygen layers of the host; there is some variation in disorientation and sharpness of the diffraction maxima of both phases for different specimens. There are indications that the spinel phase is preferentially precipitated in magnesian olivines, with the hematite phase occurring for the more iron-rich members, though both phases are usually developed in all specimens at an early stage of oxidation.

The later stages of oxidation are more difficult to study as the breakdown of the structural regularity produces increasing complexities in the diffraction effects. During the final collapse of the olivine structure, the occurrence of oriented silica and orthopyroxene structures have been tentatively identified, though in both cases it is likely that both phases occur in distorted embryonic form.

6. "Electron-probe study of a metasomatic reaction", by R.G. Burns and S.O. Agrell, Dept. of Mineralogy & Petrology, Cambridge Univ.

The development of the electron microprobe X-ray analyser has made it possible to analyse non-destructively several elements simultaneously in minute amounts of material (as small as one cubic micron or one micro-microgram) on the surface of a solid specimen. Electron-probe analysis, therefore, is particularly suitable for detecting microsegretation, exsolved phases, new microscopic phases, and for tracing compositional variations between adjacent crystals, zoning within individual crystals, and element fractionation between coexisting phases. It is possible from electron-probe measurements to establish growth patterns of crystals, and to trace distances and amounts in which various elements have migrated through a crystal structure during solid-state reactions. Such information is useful mineralogically for determining mechanisms of solid state diffusion, crystal growth, and mineral paragenesis.

An electron-probe study has been made of a thermally metamorphosed basaltic lithomarge (weathered basalt), a xenolith (10mX3mX3m) of which was enclosed in basalt magma. Thermal metamorphism of the clay minerals of the lithomarge yielded a mullite-spinel-ileminite-cristobalite (or corundum) hornfels in the xenolith. This mineral assemblage has undergone metasomatism in the vicinity (25-300mm) of the basalt contact through an interchange of Na, Mg, Al, Si, K, Ca, Ti, Cr, Mn, Fe, Co, and Ni between magma and xenolith. Mineralogical changes are the appearance of plagioclase feldspar, and of cordierite and hypersthene towards the contact. The latter minerals have developed at the expense of mullite and some spinel. Electron-probe measurements reveal that all mineral phases are zoned. A new mineral, ferropseudobrookite, has also been identified.

7. "Reduction of crocidolite by carbon monoxide", by W.E. Addison and A.D. White, Univ. of Nottingham.

Carbon monoxide reacts with the amphibole mineral crocidolite, $Na_2Fe_2^{III}(Mg, Fe^{II})_3 Si_8O_{22}(OH)_2$, at temperatures above 350°. Crocidolite is reduced and carbon dioxide is evolved, though the yield is always much less than quantitative.

There is evidence that three processes occur simultaneously: (1) a reduction of iron(III) to iron(II) which is probably a surface reaction only as it proceeds only to a limited extent; (2) a reduction of iron(II) to a lower oxidation state, i.e. the reduction of crocidolite by hydrogen; (3) interaction of carbon monoxide with the reduced crocidolite to form a carbonyl derivative. This last reaction accounts for the non-quantitative yield of carbon dioxide. The carbonyl derivative found in (3) is stable to high temperatures but reacts with oxygen to liberate carbon dioxide quantitatively.

p.m. Session on Reactions of Oxides, Carbides and Nitrides, High Temperature Oxidation and Reductions.

1. "Influence of water vapour on thermal decompositions and oxidation reactions", by W. Feitknecht, Institut für Chemie, Universität, Bern, Switzerland.

When hydroxides are decomposed, the texture of the oxide grains formed may be influenced not only by the structure of the hydroxide, but also by the pressure of the water vapour. Consider the dehydration of β- and γ-$Zn(OH)_2$. Under all circumstances the reaction is topochemical, that means the zinc oxide grains are pseudomorphs of the hydroxide crystals. β-zinc hydroxide has a layer structure and crystallizes in platelets. The crystallites of the oxide formed by decomposition in a vacuum or under a pressure of one atmosphere are not oriented. Only when decomposed in the electron beam of the electronmicroscope, the reaction is topotactic and the oxide crystallites are highly oriented.

If the rodlike crystals of γ-$Zn(OH)_2$ with a chain structure are decomposed under atmospheric pressure, oxide pseudomorphs with unoriented crystals result. Decomposed in vacuum, the oxide crystals are oriented, the [110] axes being parallel to the longest axes of the hydroxide crystals and the (001) plans more or less perpendicular to the electron beam.

When oxide hydroxides are heated different reaction products may be formed under a low or a high pressure of water. δ-FeOOH decomposes at low pressure to α-Fe_2O_3; under higher pressure it may go over to α-FeOOH. This effect, first found by Francombe and Rooksby, is being studied more closely for different preparations of δ-FeOOH. In both cases the lattice of the δ-FeOOH changes continuously, i.e. in a one phase reaction into the lattice of either α-Fe_2O_3 or α-FeOOH. These transformations are followed by X-ray and electron diffraction as well as infrared spectroscopy. γ-MnOOH decomposes at low pressure according to Verwey and de Boer to γ-Mn_2O_3, crystallizing in a defect Mn_3O_4 structure. We found that at temperatures of approximately 225° in a first step a hitherto unknown modification of Mn_2O_3 is formed (β-Mn_2O_3). Under prolonged heating it changes to γ-Mn_2O_3. Heated under conditions such that a vapour pressure up to ~1 at. may build up, the γ-MnOOH decomposes into a mixture of Mn_3O_4 and Mn_5O_8 according to the reaction (8 γ-MnOOH → Mn_3O_4 + Mn_5O_8 + 4 H_2O).

The influence of water vapour pressure is very pronounced upon the oxidation of manganous hydroxide. In very dry oxygen, the oxidation is extremely slow at room temperature. As water is formed, the reaction proceeds autocatalytically. Below a vapor pressure of about 6 torr. β-MnOOH is formed; above that a mixture of β-MnOOH and Mn_3O_4. The oxidation to β-MnOOH is topotactic; it starts from lattice defects at the surface of the $Mn(OH)_2$ platelets and proceeds along the $Mn(OH)_2$-layers. The reaction can be formulated: 2 $Mn(OH)_2$ + $^1/_2$ O_2 → 2 β-MnOOH + H_2O. Small crystals of $Mn(OH)_2$ are transformed to porous platelets composed of oriented extremely small crystallites of β-MnOOH. The oxidation to Mn_3O_4 is not topotactic nor even strictly epitactic. It seems to proceed in the thin layer of the adsorbed water saturated with Mn^{2+}- and OH^--ions and may be formulated: $3Mn^{2+}$ + $^1/_2$ O_2 + $6OH^-$ → Mn_3O_4 + 3 H_2O.

2. "Hydrothermal experiments involving Fe_3O_4, α-Fe_2O_3, and γ-Fe_2O_3", by Shoichi Kume, Mitsue Koizumi and Toshio Takada, College of General Education, Osaka Univ., Institute of Scientific & Industrial Research, Osaka, and Institute for Chemical Research, Kyoto Univ., respectively.

Hydrothermal experiments were described which illustrate the interrelationships between α-hematite, γ-hematite and magnetite under various hydrothermal conditions up to 740°C and 2 kbar pressure of H_2O.

3. "The oxidation and hydrolysis of uranium mononitride", by R.M. Dell, V.J. Wheeler and E.J. McIver, Atomic Energy Research Establishment, Harwell.

The rare-earth and actinide metals all form mononitrides which crystallize with the rock salt structure. These compounds are refractory materials, with melting points in excess of 2000°C, which exhibit metallic conductivity. The nature of their chemical bonding is imperfectly understood. Despite a superficial similarity of physical properties, the chemical reactivities of the nitrides vary enormously. Thorium mononitride (ThN) oxidises rapidly and quantitatively in moist air at room temperature, even when fabricated into an ingot; by contrast, uranium mononitride (UN) is quite stable at

100°C in boiling water, even when powdered. Other nitrides lie between these extremes. This paper reports studies of the oxidation and hydrolysis of UN and shows how the reaction mechanism is quite different from that encountered in the oxidation of elemental metals.

UN powder ignites in dry oxygen at a temperature determined primarily by its specific surface area and by the gas pressure. Just as for a metal, ignition takes place when the rate of heat liberation by surface oxidation exceeds the rate of heat dissipation. Factors such as the mass of material, its geometry and the oxygen flow rate also play a role in determining the ignition temperature. Powdered UN of surface area ~0.2-0.4 m^2/g, prepared at 1450°C, ignites in oxygen around 300°C. Between 230°C and 270°C the oxidation reaction proceeds isothermally at a rate convenient for kinetic measurements. The apparent activation energy is 31 ± 1 kcal/mole. During the reaction molecular nitrogen is released at a rate which is slow compared with the oxygen uptake. The final oxide product is amorphous UO_3 and retains some residual nitrogen; its overall composition is $UO_3 \cdot N_{0.2-0.4}$. This nitrogen is trapped within the UO_3 structure and released only with difficulty on heating. Reaction of the product with water or dissolution in acid leads to effervescence as nitrogen is liberated.

Crystallographic examination of partially oxidized UN powder reveals the presence of UO_2 and U_2N_3 as intermediate oxidation products. This surprising result led to single crystal X-ray studies being made on individual faces of large UN crystals during oxidation. It was found that the oxidized surface consisted of a sandwich structure in which a layer of U_2N_3 was formed between the UN crystal and an outer layer of crystalline UO_2. Both the U_2N_3 and UO_2 are epitaxially oriented with respect to the UN crystal, the epitaxy being such as to maintain a face-centered cubic array of U atoms common to the three phases. A reaction mechanism is suggested based upon the following steps: (1) Chemisorption of oxygen at the outer UO_2 surface, (2) diffusion of oxygen through the UO_2 via interstitial sites, (3) a solid state reaction between UO_{2+x} and U_2N_3 at the first interface; in this reaction the f.c.c. array of U atoms is maintained and it is likely that an intermediate oxy-nitride is formed (4) part of the nitrogen is released from the lattice, forms molecular nitrogen and escapes through pores in the outer UO_2 layer; part of the nitrogen dissolves in the oxide product and the remainder enters interstitial sites in the U_2N_3 lattice, (5) under the influence of a concentration gradient, nitrogen atoms diffuse through the U_2N_3 lattice to the UN interface where reaction occurs to form further U_2N_3, again maintaining the epitaxial relationship, (6) finally, the UO_2 product with its dissolved nitrogen is oxidized to UO_3.

The hydrolysis of UN takes place in water vapour (30 mm pressure) at temperatures above 300°C. With powdered UN, nitrogen is released quantitatively as ammonia according to the primary reaction $UN + 2H_2O \rightarrow UO_2 + NH_3 + \frac{1}{2}H_2$. Using single crystals it is invariably found that a sandwich structure of U_2N_3 and UO_2 is formed, as in the reaction with oxygen. The epitaxial relationship is the same for both oxidants. Mechanistically the reactions must be rather different as water will not dissolve in UO_2, nor ammonia in U_2N_3. It is postulated that water vapour diffuses through pores in the UO_2 outer layer to react with U_2N_3 at the U_2N_3/UO_2 boundary. This reaction is thought to involve free radicals

such as $NH_2^{\cdot}$, $NH^{\cdot}$, $N^{\cdot}$, The stable reaction products are NH_3, NH_2 and nitrogen atoms dissolved in the U_2N_3 lattice. These latter diffuse to the UN/U_2N_3 interface where they react as during oxidation.

The comparative stability of UN toward hydrolysis is ascribed to the protective action of a thin surface film of U_2N_3 (or oxynitride) present at the surface. The protective nature of this film is attributed to the fact that it is based on a f.c.c. array of uranium atoms and is epitaxially oriented with respect to the UN crystal. Other mononitrides which hydrolyze far more readily either do not form a higher nitride at all (PuN) or else only one based upon a different symmetry of metal atoms (Th_3N_4 - hexagonal structure).

4. "The kinetics and mechanisms of sintering of uranium and plutonium carbides", by M.B. Finlayson and S. Pickles, UK Atomic Energy Authority Reactor Group, Dounreay Experimental Reactor Establishment, Thurso, Caithness, Scotland.

The effects of variations in carbon content and of nickel sintering aids on the sintering kinetics of uranium/plutonium carbides have been investigated by measuring the shrinkage rates of compacted pellets, using a hot-stage microscope at temperatures from 1350 to 1750°C. Attempts have been made to interpret the mechanism in the light of published theories.

5. "The oxidation of nickel carbide", by J. Freel and A.K. Galway, Queen's University of Belfast, N. Ireland.

Nickel carbide reacted with gaseous oxygen 300-330° to give a total yield of carbon dioxide equivalent to that expected from the total carbon content of the sample (i.e. carbidic + the excess elemental carbon). The yield of carbon monoxide was negligible, 1.5% that of carbon dioxide and was only detected during the early stages of reaction. The carbon dioxide formation rate process was decleratory throughout, the energy of activation found was 35 ± 2 kcal $mole^{-1}$, from tangents to the α/t curve at $\alpha = 0.4$ and $\alpha = 0.6$ (α defined as the fractional decomposition). The rate of reaction was independent of oxygen pressure 50-100 mm, and only slightly slower at 25 mm (which may be due to consumption of gaseous reactant) at 300°C; rates were independent of pressure 25-100 mm at 280°C.

6. "Electrical conductivity and self-diffusion in yellow lead oxide", by A. de Beer, Y. Haven and L. Heyne, N.V. Philips' Gloeilampenfabrieken Eindhoven, Netherlands.

A study is made of the electrical characteristics of the yellow modification of PbO in the temperature range of 500° - 900°C, where it is thermodynamically stable. The electronic and ionic contributions to the electrical conductivity, which together are responsible for the reactivity of the solid with a surrounding gas atmosphere, are distinguished by means of several methods: transport measurement, emf measurement, current measurements with polarized electrodes. It appeared that a variation in the oxugen pressure as well as doping with e.g. K or Bi had a major influence on the conductivity mechanism.

To correlate the ionic conductivity component with the coefficient of self-diffusion, self-diffusion measurements were carried out with O^{18} isotope and mass-spectrometric analysis. It was found that apart from the bulk diffusion, the surface reaction of O_2 with PbO may be rate limiting. The O-isotope exchange between CO_2 and solid PbO indicates a much faster surface reaction.

7. "Kinetic studies at high temperatures using an electron microbeam probe mass spectrometer", by T.J. Gray, S.F. Hulbert and L.N. Kowalczy, State Univ. of New York College of Ceramics at Alfred Univ., Alfred, New York.

The kinetics of high temperature vaporization are of profound importance for material evaluation where their use is extended to the very limits of present knowledge. For these studies a mass spectrometer was designed and constructed with which it is possible to identify and measure quantitatively species arising during vaporization processes occurring from solids as a function of time. This technique, however, is limited to the investigation of the net effect integrated over the whole surface whereas it is believed that grain boundaries probably contribute predominantly or at least to a disproportionate extent. In order to investigate this aspect it was decided to design and construct a novel source for the mass spectrometer comprising an electron micro-beam probe which could be used to scan the surface for display and analysis and then subsequently be used as a selective electron beam heater to volatilize grain boundary regions.

The mass spectrometer itself is of a Nier type, containing a 60°, 12 inch magnet with a pole face gap of 7/8 inch, continuously variable to 11,000 gauss. The original and interchangeable source is a combination thermal ionization/electron affinity type, achieved by providing for the voltage applied to the accelerating plates to be reversed. The detector presently used consists of the first dynode of a photomultiplier tube as an ion detector, delivering a signal to a commercial model vibrating reed electrometer. The sensitivity of this combination is of the order of 10^{-17} amps detectable.

In a thermal ionization source the probability of a positive ion of a given species being evaporated from the surface is given by the Saha-Langmuir expression,

$$n_+ = n_o e^{e(w-\phi)/kT}$$

where n_+ is the number of positive ions of that species produced, n_o is the total number of atoms (molecules) of the given species which are evaporated, w is the work function of the surface, and ϕ is the ionization potential. A similar equation governs electron affinity sources, in which negative ions are examined. w and ϕ are both functions of temperature and the dependence is usually unknown, especially within temperature ranges of interest in vaporization studies. It is therefore necessary to monitor and control temperatures of the source very precisely. This is accomplished by means of an optical pyrometer focused on a very small area (approximately 2 mm diameter) and equipped with dual interference filters to increase precision.

A typical kinetic study is exemplified by the dissociation and sublimation of TiO_2. The following reactions contribute:

$$TiO_2 \rightarrow TiO_{(2-x)} + \frac{x}{2} \cdot O_2$$

$$TiO_2 \rightarrow Ti_2O_3 + \frac{1}{2}\ O_2$$

$$TiO_2 \rightarrow TiO_{2(vap)} + TiO_{(vap)} + \frac{1}{2}\ O_2$$

Negligible quantities of $Ti_{(vap)}$ were observed in the mass spectrometer over the temperature range investigated. From the cumulative data it may be concluded that TiO_2 initially loses oxygen from point defects, while above approximately 1500°K a secondary process is observed with the sublimation of TiO_2, TiO and a trace amount of Ti. The activation energy for the evolution of oxygen is 34 Kcal from 1115°K to 1500°K while that for the sublimation process above 1500°K is 55 Kcal with a net apparent value of 30 Kcal, all to a precision of ± 7% cumulative.

This technique provides data integrated over the entire surface of a relatively massive polycrystalline sample but provides no specific information on local reactions which may be occurring at grain boundaries. For this reason a more sophisticated system has been designed and constructed which should permit a detailed study of "localized" kinetics. To achieve this goal, an electron microbeam probe has been coupled to the source of the mass spectrometer.

In conventional use the electron microbeam probe, originally developed by Castaing, Coslett and others provides topographical and analytical data for surfaces derived from the specimen current, back-scattered electrons and X-rays generated when an electron beam of diameter approximately 1μ scans the specimen surface. In the electron microbeam mass spectrometer source the beam is produced by a four lens compression system of electron optics as described by Birks producing a parallel beam of electrons 0.5 to 5μ in diameter with theoretical focus at infinity rather than the point source generally employed in devices of this type. This technique permits the use of a relatively long working distance between the pole face of the final lens and the sample, and provides a much higher than average beam current. Electrostatic deflection circuits are provided to permit visual display while the specimens can be positioned mechanically. Back-scattered electrons are detected by a MOS-FET detector-preamplifier instead of the more conventional fluorescent material and photomultiplier resulting in greatly improved signal-to-noise ratio and facilitating higher scan rates to improve image definition. Conventional bent crystal monochromators and flow proportional counters are incorporated for analytical purposes using standard X-ray fluorescence techniques. The mass spectrometer itself, however, can also be used for the analysis of light elements possessing a considerable advantage over the multilayer lead stearate type grating.

While the essentially conventional electron microprobe is employed for surface analysis, the three-dimensional mechanical drives permit the exact positioning of any point on the specimen surface at the source of the

mass spectrometer. Under these conditions, the power of the electron beam can be increased to promote volatilization from a localized area, supplemented where necessary by a furnace incorporated at the sample stage. In this manner, vaporization of a region of the order 1.3μ can be accomplished.

8. "On the mechanism of decomposition in a reducing atmosphere of carbonato-pentamminocobalt(III) nitrate leading to cobalt powders of varied morphology", by M. Figlarz, Laboratoire de Chimie des Solides, Université de Paris.

Cobalt powders have been prepared by the decomposition of carbonato-pentamminocobalt(III) nitrate in a current of reducing gas (N_2 or $N_2 + H_2$) at 350°C. The reaction and its products were studied using X-ray diffraction, nitrogen adsorption, electron microscopy, infrared spectra, DTA, and TGA. Depending on the rate of supply of the reducing gas, either hexagonal cobalt, or mixtures of the hexagonal and cubic polymorphs were obtained. The powders rich in the cubic form appeared as small, primary, monocrystalline grains, while those rich in the hexagonal form appeared to have undergone sintering.

At low supply rates of the reducing gas diffusion plays a dominant role in the reaction zone. NH_3 is lost and CoO formed. The gaseous environment hinders access of H_2 and loss of the water vapour formed at the reaction interface. These conditions favour the formation of the metal crystals by epitaxy or oriented overgrowth on the CoO.

Wednesday, 13 July

a.m. Diffusion Studies; Reactions Influenced by Radiation; Effects of Mechanical Damage.

1. "Self-diffusion and solid state reactions", by R. Lindner, Chemistry Department, CCR Euratom, Ispra, Italy.

2. "Microcrystalline phases in silicate glasses: structures and kinetics of formation at high viscosities", by Doris Evans, Corning Glass Works, New York.

Glasses constitute such a widely variable structural and compositional family that generalizations, other than operational and negative ones, cannot readily be made. They are inorganic products of fusion which cool to a rigid condition without crystallizing. They are as continuously connected as crystalline solids and they have the same local environment of atoms about a given atom. As the distance from an arbitrarily chosen reference atom is increased, the atomic population statistics become indefinite; neither the number of atoms nor their distances away from the reference atom is reproducible throughout the mass. This absence of long-range order is the liquid-like feature of glass structure. The statistical spread in what we might visualize as classes or regions with different degrees of connectedness is reflected in the continuous variation of viscosity with temperature. Besides being the basis of glass working operations, the viscosity-temperature characteristic distinguishes the glassy state as a fourth state of matter. Viscosity provides, in effect, a variable time scale for studying reactions within a glass or between it and the environment.

These reactions range from liquid-like unmixing to crystalline solid-like, diffusion-controlled reactions and phase transformations. The former area has been emphasized in recent studies and striking examples of liquid-liquid unmixing obtained. It is therefore tempting to extrapolate bulk liquid concepts down to a submicroscopic scale of "droplets" whose formation defines the first stage of structural rearrangement in glass.

The term "droplet" seems now to be suffering the same fate as did the term "crystallite" in early controversies concerning the nature of glass structure. The concept of a drop is now often scaled down to dimensions where it no longer has any clear physical meaning. Both "droplet" and "crystallite" are alike in implying that the volumes so described are sufficiently large to exhibit liquid or crystalline properties such as interfacial tension or a diffraction pattern. Volumes which contain too few atoms to display the cohesive forces of a drop or the periodic arrangement of a crystal cannot meaningfully be described as miniature versions of either. Such volumes must be viewed statistically as clusters of atoms and they will have a statistical distribution of size as well as composition for any glass. They are the embryo of classical nucleation theory and those which are above a certain critical dimension and atomic population will have internal bonding forces large enough to insure survival and growth to stable nuclei.

If cohesiveness is the only property distinguishing such nuclei, then clearly they will evolve as drops of a liquid phase while the additional property of ordered distribution of atoms defines the precursors of crystallites.

Several examples of pre-crystalline reactions within silicate glasses at high viscosities will be cited. The continuous isothermal growth of clusters, confirmed as crystalline on the scale of 60-80A, reveals structures and compositions that are unique.

There is much of fundamental importance to be learned by following reactions in glass and many surprises are in store for us due in large measure to the statistical nature of glass structures and the role viscosity plays in sorting out reactions. A particular formation must be both geometrically accessible at regions within the glass and thermodynamically favored if we are to observe it; it need not, however, be favored over other arrangements which become available only at somewhat lower viscosities and higher temperatures. The "wrong" structure for a compound may have a transitory microcrystalline existence in glass and transform gradually to the normal structure established for well-crystallized versions formed in a totally different environment, or it may fall victim to competitive reactions.

The intricacies of the reactions reveal a world of possibilities that link the solid, liquid and gas states.

3. "Surface diffusion studies on ceramic oxides", by J.W.S. Jones, J. Henney and D.T. Livey, Atomic Energy Research Establishment, Harwell, Berks., England.

Surface diffusion processes have been studied in uranium oxide and magnesium oxide over the temperature range 1000°C to 1500°C in different atmospheres using grain boundary grooving and scratch smoothing as the experimental methods of measurement.

4. "Cation self-diffusion in neutron irradiated beryllium oxide", by H.J. de Bruin, Australian Atomic Energy Commission, Research Establishment, Sutherland, New South Wales, Australia.

A considerable enhancement in cation tracer diffusion rates has been observed in irradiated BeO, compared with normal thermal transport in unirradiated polycrystalline specimens. For the latter it has been established that cation vacancies are the diffusing species. The enhancement of diffusion in irradiated material is attributed to an interstitialcy mechanism.

At temperatures above 1200°C virtually no enhancement is observed, but below 750°C the radiation induced Frenkel disorder is sufficiently stable to contribute considerably to diffusion rates. At 750° - 1200°C annihilation of the interstitials takes place at rates comparable with that of diffusion. Consequently diffusion coefficients are time dependent.

The activation energy at low temperatures in irradiated BeO is less than half that for unirradiated specimens and the diffusion coefficients at 500°C after irradiation are comparable with those at 1200°C on the standard curve ($\approx 10^{-12}$ $cm^2/sec.$).

Both Be and He (from n radiation) diffusion studied. Irradiation beam up to 10^{19} n/cm^2.

5. "Reactivity of tritium formed by $^6Li(n,\alpha)^3H$ nuclear reaction in crystalline lithium compounds", by T. Costea and Constanta Mănţescu, Institutul de Fizică Atomică, Căsuţa Poştală 35, Bucharest, Romania.

By irradiating lithium compounds in the reactor tritium atoms are produced in considerable quantity as a consequence of the large cross-section for the $^6Li(n,\alpha)^3H$ nuclear reaction. The behavior of the recoiling tritium atoms is important for both theoretical and applied chemistry.

A way to obtain information about the behavior of the recoil tritium produced in crystalline lithium compounds was suggested by the authors. It consists of heating the irradiated compounds and observing the radioactivity of the gaseous fraction released as a result of the thermal treatment, the radioactivity retained in the crystals being determined after the dissolution of the thermally treated samples. In this manner the following compounds were studied: LiF, LiCl, LiBr, LiI, $LiNO_3$, Li_2CO_3, Li_2CrO_4, $LiAlH_4$, NiO(5%Li_2O).

6. "The influence of γ-radiation and of admixed solids on the thermal decomposition of zinc formate", by P.L. Evans, F. Solymosi and F.S. Stone, Department of Physical Chemistry, The University, Bristol 8, England.

Zinc formate crystallizes as the dihydrate. The water of crystallization begins to be evolved at ~100°C., but the anhydrous salt is stable up to 240°. Above this temperature thermal decomposition giving rise to zinc oxide and a variety of gaseous products, including CO_2, CO, H_2, H_2O and HCHO, has been reported in the literature. In the present work two new aspects of the decomposition have been studied. First, the influence of γ-radiation has been investigated, both prior to the decomposition and during decomposition, and secondly the effect of several admixed solids has been examined. Knowledge of th. kinetics of the decomposition of the pure solid has also been extended by isothermal studies between 250° and 300°C.

7. "Thermal decomposition of irradiated lead nitrate", by S.R. Mohanty and M.N. Ray, Banaras Hindu University, Varanasi-5, India.

Ground AR grade lead nitrate was dried in a vacuum desiccator over phosphorus pentoxide. Samples sealed in vacuo in glass ampoules were irradiated with ^{60}Co gamma-rays to a dose of 100 Mrad at the dose rate 1.5 Mrad/hr. Thermal decomposition was studied at different temperatures in the range of 380-425°C and was followed by measurement of the gas pressure developed with a fluorocarbon oil manometer.

The pressure-time curves are sigmoid in nature without any induction. The effect of irradiation is to enhance the decomposition rate. For example, the unirradiated material developed 1.63 cm pressure on 80 minutes heating at 390°C and the irradiated material 2.65 cm. The corresponding values at 415°C were 12.06 and 13.70 cm respectively.

The decomposition is represented by the Prout-Tompkins equation: $\log p/(p_f-p) = kt + c$, with different constants k_1 and k_2 for the acceleratory and the decay stages respectively. The activation energy for the acceleratory and the decay stages are, respectively, unirradiated 60.1 and 11.7 kcal $mole^{-1}$, and irradiated 62.9 and 14.3 kcal. The activation energy is thus not appreciably affected by irradiation.

Of the three mechanisms by which gamma-rays interact with matter, viz. the photoelectric effect, the Compton effect, and pair production, the Compton effect has the largest cross section for ^{60}Co gamma-rays except in the case of materials of high atomic number where some photo-electron emission and pair production also occurs. Electrons from these events are not capable of displacing lead. Production of displacements by either the Varley or the Seitz mechanism does not also seem important in the case of the nitrates. Excitation and ionization of the nitrate ions, however, produces chemical damage. These damage species constitute decomposition nuclei and are responsible for the higher thermal decomposition of the irradiated crystals.

8. "Triboabsorption of noble gases", by G. Heinicke and M. Friedrich, Institut für Physikalische Chemie, Deutsche Akademie der Wissenschaften zu Berlin, 1199 Berlin-Adlershof, Rudower Chaussee 5, West Germany.

The mechanical and chemical interactions of the frictional components with each other and with the surrounding atmosphere are very important for the processes of friction and wear. According to the investigations of Thiessen, Heinicke and Meyer, a shortlived, highly active state with magma-plasma character results from the mechanical stressing of solids. Simultaneously the gas present in bulk will be excited. Chemical reactions occur and a definite amount of gas enters the disordered lattice of the solid. The use of noble gases is to be recommended in studying these kinetic processes. With radioactive isotopes it is possible to study the processes of absorption and desorption for a single impact. Gases absorbed in the lattice can also be desorbed by annealing the solid. The kinetics of these processes permit one to draw certain conclusions concerning the nature of the defects in stressed lattices.

Thursday, 14 July

a.m. Session on Diffusion, Kinetic, and Thermodynamic Studies; Zeolites, Glasses, Cyanides, and Metals.

1. "Cation exchange in crystalline aluminosilicates as a solid state reaction", by R.M. Barrer, Chemistry Department, Imperial College of Science & Technology, London, S.W.7.

Zeolites and felspathoids all have structures which are sufficiently open for the cations to migrate rather freely within the anionic frameworks. Often, in addition to the mobile cations necessary to neutralize the negative charge of the framework, water (zeolites) or salt molecules (felspathoids) fill the remaining intracrystalline pore space. The ion-exchange capacities are very high. The distinction between zeolites and felspathoids is relatively artificial: in the zeolites, the water molecules may be replaced by salts; in the felspathoids the salt molecules may be replaced by water.

The frameworks in zeolites or in felspathoids differ in the extent to which they can adjust themselves to cations of different sizes, and although the dimensional changes in this adjustment are not as great as in the layer silicates such as smectites, illites or vermiculites, these dimensional changes can result in notable alterations in the exchange phenomena observed. Where the anionic frameworks exhibit negligible adjustment, there is usually continuous mutual solid solubility between the end members of the exchange, and thus continuous exchange isotherms result. The diffusion kinetics correspond with cation migrations down continuous concentration gradients.

On the other hand, if lattice adjustment becomes sufficiently marked, there may be immiscibility gaps between the end members of the exchange, and the isotherms accordingly show discontinuities. Nucleation now occurs, and hysteresis may be found accompanied by remarkable history-dependent behaviour. The several kinds of system in which continuous or limited solubility may occur give rise to four main kinds of exchange isotherm which can all be described in terms of a treatment that also leads to Kielland's equation.

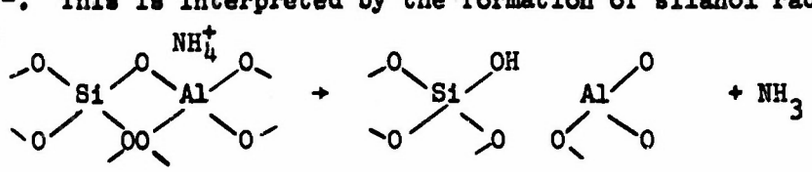
Selectivity in exchange is controlled by several factors. One of these is ion sieve action: some cations cannot penetrate the crystal because they are too large to pass the mesh of the anionic framework; in other situations the ions may pass the mesh but on account of their size they would at complete exchange more than fill the available intracrystalline space. These are not the only factors which are involved, and selectivity can be exceptionally good in exchanges involving specific ion pairs.

In several zeolites, differential heats of exchange have been measured as functions of amount of exchange, and standard heats, entropies and free energies of exchange have been determined. Heats and entropies of mixing of the end members of the exchange have also been derived. The sequence of the heats can often be predicted in terms of a model in which exchange solution and crystal are regarded as inert dielectrics.

Diffusion in a zeolite or felspathoid is describable in terms of an inter-diffusion coefficient, two intrinsic diffusion coefficients (one for each ion), and two corresponding self-diffusion coefficients. Even the self-diffusion coefficients may depend strongly on the cationic composition of the exchanger, but the relations between all the diffusion coefficients have been derived by the irreversible thermodynamic method of treating forces and fluxes.

2. "Proton delocalization in decationated zeolites", by J.B. Uytterhoeven, R. Schoonheidt and J.J. Fripiat, Université de Louvain, Héverlé-Louvain, Belgium.

Fripiat, Rouxhet and Jacobs have shown that the intensity of the fundamental vibrations of micas decreases with increasing temperature. In order to explain this phenomenon they suggested that dehydroxylation is preceded by a reversible process described as a delocalization of constitutional protons. This conclusion was reached by demonstrating that the OH dipole orientation does not change upon heating and that the shift in the proton population towards higher vibration energy levels at higher temperature is too low to explain the phenomenon. An attempt was then made to extend these observations to other mineral structures, especially those with catalytic activity. Since the acidity of silicoalumina surfaces is due either to Brönsted or Lewis sites, and the transformation from the first into the second type of sites is related to proton removal, it appeared worthwhile to investigate the existence of a possible proton delocalization process in this class of materials. Uytterhoeven, Christner and Hall have shown that NH_4-X and NH_4-Y zeolites treated progressively to 300° lose ammonia whilst two well defined OH stretching bands appear at 3660 cm^{-1} and 3580 cm^{-1}. This is interpreted by the formation of silanol radicals as follows:



the differentiation between the two bands being due possibly to two different locations or orientations of OH dipoles. The decationated forms obtained upon heating are catalytically active in cracking hydrocarbons.

Actually the transformation of the original Na-X or Na-Y zeolites into the ammonium form by cation exchange is never complete and the solid contains a variable proportion of Na. Moreover, a fraction of ammonium cations is lost on drying the sample at 110°C before the chemical analysis. As the catalytic activity of zeolites is to some extent similar to that of silico-alumina cracking catalysts, the surface was considered as acid. From this viewpoint it is obvious that any process able to promote proton mobility may aid in explaining the catalytic behavior.

3. "The exchange between water and analcite", by A. Dyer and A. Molyneaux, Royal College of Advanced Technology, Salford 5, Lancs., England.

4. "The Diffusion of water in soda-lime glass", by M.H. Stacey, Mond Division, Imperial Chemical Industries, Ltd., Runcorn, Cheshire, England.

The diffusion of water into glass specimens 1 mm thick has been followed by means of water labelled with tritium. The technique was similar to that described by Drury & Roberts with modifications appropriate to the different temperature range (up to 400°C) and pressure range (10^{-3} to 1 mm water vapor pressure). The specimens were sectioned to determine the distribution of tritium as a function of distance. As the penetration was generally less than 2μ sectioning was by step-wise etching in 1% HF. This gave the distribution in the form of a histogram. Values of diffusion coefficients as a function of water concentration were derived from the smoothed distribution curve by Matano's method.

5. "Kinetic studies of low-temperature, hydrogen-bonded glasses", by Juan A. McMillan, Argonne National Laboratory, Argonne, Illinois.

The kinetics of glass relaxation and crystallization of supercooled phases of hydrogen-bonded compounds like water, hydrazine, u-dimethylhydrazine, and alcohols is currently under study in our laboratory. Thermal studies of pure compounds and of binary mixtures have permitted the evaluation of activation barriers for glass relaxation and for crystallization. In the latter case, it is possible to distinguish between nucleation-controlled and dislocation-controlled rate processes, by measuring the apparent entropy of activation. Further results, compared with values derived from viscosity measurements, indicate that the activation energy for growth of pure, supercooled hydrazine monohydrate on hydrazine crystals is 30% smaller than the activation energy for self-diffusion.

6. "Phase transitions and thermodynamic properties of alkali and thallous cyanides", by H. Suqa, T. Matsuo, M. Sugisaki and S. Seki, Department of Chemistry, Osaka University, Toyonaka, Osaka, Japan.

There are known considerable numbers of ionic crystals which consist of spherical cations and spheroidal anions and crystallized in the NaCl or the CsCl type cubic form at room temperatures. This fact may indicate that the non-spherical anions in these crystals have an apparent spherical symmetry due to some orientational disorder to satisfy the lattice symmetry. Accordingly these crystals may undergo one or more phase transitions to the other forms with lower symmetry than the cubic one when they are cooled down. As one of the simplest cases we have been studying the thermodynamic behaviors of NaCN, KCN and RbCN crystals having the NaCl type and also of CsCN and TlCN crystals with the CsCl type at room temperature.

In a previous paper we have reported some thermodynamic properties and discussed the nature of phase transitions of KCN crystal. In the present paper we have extended our study to the above-mentioned cyanide compounds for the purpose of elucidating the effect of variation in the size of cations on the ordering process of cyanide ion.

Experimental

(a) Sample. The samples of Rb-, Cs- and Tl-cyanides were prepared by the addition reaction of the respective hydroxides with HCN. These cyanides thus obtained and also Na- and K-cyanides (Merck Reagent, G.R.) were recrystallized from the alcoholic solutions and then dried in vacuum (10^{-5} Torr.) for several hours at 120°C.

(b) Apparatus and Procedures. Measurements of the heat capacities were carried out in the temperature range from 12° to 330°K by use of the adiabatic calorimeter equipped with the two-fold adiabatic shields and sample container made of gold-plate and platinum fins. The adiabatic conditioning was performed with the aid of automatic controlling electronic system within a millidegree of temperature. The temperature of the container was read on the platinum resistance thermometer calibrated at the NBS of the United States.

Result and Discussion

In the following we should like to distinguish their thermal behaviors in three groups and discuss them separately. First of all, we may compare the results of KCN and of NaCN crystals. These crystals show two types of phase transition. Taking into consideration the X-ray data on their crystal structures, the theoretical calculation by Matsubara and Nagamiya and also our thermal data of entropy change associated with the phase transitions, we may conclude that the lower phase transition of both crystals is ascribed to the end-for-end reorientational process of the cyanide ion in the crystal. With regard to the possible arrangement of the anions for the lowest temperature phase, our numerical calculation of the dipole-dipole interaction energy suggests strongly that the polar arrangements of anions along the orthorhombic b-axis (space group C_{2v}^{20}-Imm2) is the most stable one.

In contrast to the cases of KCN and NaCN, RbCN and CsCN show only a single anomaly in their heat capacity curves. The room temperature modifications of NaCN and KCN crystals are shown to have the configurational entropy equal to Rln 8 which comes from the equivalent potential minima referred to the orientational entropy will be lost stepwise through the two phase transitions to zero value at the lowest temperature phase where the most stable orientation of anion seems to be realized rather easily. On the other hand, the magnitude of entropy of transition of RbCN or CsCN is too small to account for the decrease of configurational entropy in the same sense as was explained in the two salts mentioned above. Presumably, this difference is caused by the disordered arrangement of anion in these salts at the lowest temperature owing to the few possible orientations with nearly equal potential wells for anions which are assumed reasonably by considering the crystal structure of this phase.

7. "Effect of interstitial and substitutional impurities on diffusion in Nb-Ti", by D.J. Nagel and L.S. Birks, U.S. Naval Research Laboratory, Washington, D.C. 20390.

Controlled amounts of interstitial elements (O_2 and N_2) and substitutional elements (Co, Sn, Ag, Mo) have been added to the Nb-Ti system. Three effects of the added impurities are being studied: (1) Variation of the grain boundary diffusion of Ti into Nb and Nb into Ti; (2) Variation in the diffusion coefficient itself; (3) Discontinuity in the diffusion coefficient at the α-β Ti phase boundary which depends on the impurity content. Results of the initial tests with O_2 and N_2 can be summarized as follows: In the Nb-Ti system the diffusion coefficient varies from 10^{-9} cm^2/sec at 10 A % Nb to 10^{-12} cm^2/sec at 90 A % Nb. The Ti diffuses about 90 microns into the Nb in 24 hours at 1100°C but the Nb diffuses over 600 microns into the Ti in the same length of time.

8. "The investigation of atomic steps in diffusion by means of field ion microscopy", by D.W. Bassett, Imperial College of Science and Technology, University of London.

A study has been made of certain displacements of tungsten atoms on a clean tungsten surface. Movement between (111) type kink sites along the edge of (011) terraces required an activation energy of 1.8 eV, while for jumps between kink sites of (001) type, the activation energy was 2.1 eV. Atom movement along the edges of (111) and (001) terraces required activation energies of 2.2 eV and 2.3 eV respectively. These values are much lower than energy barriers to surface atom jumps, (>3eV) calculated from a simple broken bond model of the surface.

p.m. Session on Solid-Solid and Solid-Gas Reactions; Optical and Electron Microscope Studies; and Other Topics.

1. "Solid state reactions and phase equilibria in the system $MgO-FeO-Fe_2O_3$", by P. Reynen, N.V. Philips Research Laboratories, Gloeilampenfabrieken Eindhoven, Netherlands.

The solid state reaction $MgO+Fe_2O_3 \rightarrow MgFe_2O_4$ has been studied with the aid of diffusion couples and also using the data from the ternary phase diagram which was reinvestigated in the present study. The solid state reaction mentioned above proceeds by solid state diffusion of the cations through the reaction layer and by transport of oxygen via the gas phase.

The reaction velocity depends on temperature and partial oxygen pressure but also on pure geometrical factors, which determine the number of contact points between MgO and Fe_2O_3 particles. At these contact points a reaction layer is formed over which a concentration gradient is built up, because the compositions at the spinel/Fe_2O_3 boundary and at the spinel/MgO boundary are different, as indicated by the phase diagram. The concentration gradients over the reaction layer are the driving forces for the reaction. The reaction velocity will thus depend on the magnitudes of these gradients which are determined by the compositions at the phase boundaries, and the thickness of the layer already formed. Due to a certain ion mobility these concentration gradients lead to a diffusion of ions. The ion mobilities are determined by the composition of the reaction layer, number and kind of defects and temperature. The overall reaction velocity is thus a very complex quantity. Ternary phase diagrams published before, show that the stoichiometric composition $MgFe_2O_4$ lies in a two-phase region. No such anomalous behavior has been found in the present study.

A number of interesting phenomena concerning the ternary diagram have been studied, such as the existence of metastable solid solutions of Fe_2O_3 in the spinel phase and the segregation of α-Fe_2O_3 from that phase. Further, the boundaries of the spinel field, the form of the isotherms and the defect structure of compositions lying in the spinel field have been determined. The experimental data have been obtained by thermogravimetric analyses.

2. "Solid state reactions between mercurous halides and iodine", by R.P. Rastogi and R.L. Dube, Gorakhpur University, Gorakhpur, India.

A study of solid state reaction kinetics has been made for the systems mercurous chloride and iodine and mercurous iodide and iodine. The reactants were taken in capillaries, first in contact with each other, and then with air-gaps of varying length between them.

The kinetic data for the reaction between Hg_2Cl_2 and I_2 in contact with each other are best represented by an equation $\xi^2 = 2k_1te^{-p\xi}$ where ξ is the thickness of the product layer, t is the time of reaction and k_1 and p are constants; k_1 is temperature dependent and p is independent of t. A similar equation has been found to hold good when the reactants are separated by small air gaps, the only difference being in the values of the constants (k_1' and p' corresponding to k_1 and p).

The reaction between Hg_2I_2 and I_2 in contact with each other is such that another relationship, $\xi^2 = kt^n$, is the most suitable. Here k and n are constants; the former depends on temperature and the latter is

independent of it. In presence of an air gap another relation holds good: $\xi^2 = k''t+c$, where k" and c are constants.

The constants k_1' and k" in the two cases are related to the length of the air gap, d, in the following way: $k_1' = c'e^{-n'/d}$ and $k'' = c''e^{-n''d}$; n', n", c' and c" are constants.

The mechanism of lateral diffusion for the reaction between Hg_2Cl_2 and I_2 appears to involve vapour-phase diffusion, since the energy of activation is nearly equal to the heat of sublimation of iodine and for the reaction between Hg_2I_2 and I_2 surface migration, since the energy of activation is only 3.07 kcal deg^{-1} $mole^{-1}$. Gravimetric studies show that during the inward penetration of the grain, bulk diffusion takes place in both cases. In this case, the energies of activation were found to be 25.0 kcal $deg^{-1}mole^{-1}$ and 23.77 kcal $deg^{-1}mole^{-1}$.

The stoichiometry of the two reactions has also been established in the two cases which proceed as follows:

$$Hg_2Cl_2 + I_2 = 2HgClI \quad \ldots \quad (1)$$

$$Hg_2I_2 + I_2 = 2HgI_2 \quad \ldots \quad (2)$$

This is the first report of the formation of HgClI in the solid state.

3. "Dislocation mechanisms in solid state reactions", by B. Hyde, University of Western Australia, Nedlands, W. Australia.

4. "The effect of crystal size on the decomposition of crystals: sodium and thallous azide", by R.F. Walker, N. Gane and F.P. Bowden, Dept. of Physics and Chemistry of Solids, Cambridge Univ., England.

Methods have been developed for the preparation of very small crystals of uniform size and these, coupled with ultra-high vacuum techniques, have been applied to the study of the kinetics of the slow decomposition of sodium and thallous azides. Measurements were made at three different crystal sizes ranging from 2 mm to 2μ diameter and over a range of temperatures. The technique made possible the use of extremely small sample sizes (about 0.1 micrograms).

The decomposition of both substances occurred in two principal stages, an initial decelerating stage leading to an induction period and a final stage in which the rate of decomposition accelerated to a maximum nearly linear rate. The extent of decomposition in the initial stage and the maximum rate of decomposition in the final stage were found to be approximately proportional to specific surface area.

The course of the decomposition in the larger crystals was followed by optical and scanning electron microscopy. This revealed that decomposition

took place by interface reaction which proceeded into the crystals in directions parallel to the layer structure of the crystal lattices.

An interesting technique was described for the production of crystals of extremely small total sample size.

5. "The thermal decomposition of some precious metal compounds", by M. Seal and M. Kranitz, Engelhard Industries, Inc., Newark 5, New Jersey.

Using electron microscopy and diffraction we have studied the thermal decomposition of two precious metal salts, potassium chloroplatinate (K_2PtCl_6) and ammonium chloroplatinate ($(NH_4)_2PtCl_6$). These salts decompose when heated to temperatures above about 250°C yielding metallic platinum, chlorine, and potassium or ammonium chloride. Two methods were used in the investigation. In the first, crystals of the chloroplatinate were deposited on a suitable substrate, either from suspension or by evaporation of a drop of solution. Samples prepared in this way were then heated in air to selected temperatures. After the samples had cooled, shadowed replicas for electron microscopy were prepared. Undecomposed salts were removed from the replicas by solution in water, but platinum crystallites remained and their relationship to the salt crystals was studied with the electron microscope. Temperatures of heat treatment ranged from room temperature to 400°C (where decomposition was complete in a very short time). Nucleation and growth of the crystallites was studied. Substrates used included glass, mica, and sapphire, and the influence of substrate on the crystallization of the salt was investigated.

In the second method small crystals of the chloroplatinate supported on carbon films were examined directly in the electron microscope. The crystals were decomposed by increasing the electron beam intensity and the change was studied by microscopy and diffraction. There was no evidence of intermediate structures occurring during decomposition, and no preferred orientation of the platinum crystallites were observed.

We have concluded that decomposition of these salts occurs in a disordered manner with migration of platinum atoms over comparatively large distances to the nuclei of crystallization. This contrasts with the more ordered mode of thermal decomposition reported by other workers for a number of other compounds, e.g. silver azide, magnesium hydroxide.

Similar studies of other precious metal compounds, in particular on the thermal decomposition of gold ethyl mercaptide, are being carried out.

6. "Electron microscope studies of reactions between calcium carbonate polymorphs and fluoride ions", by J.M. Bennett and J.A. Gard, University of Aberdeen, Old Aberdeen, Scotland.

7. "Polymorphic transitions and orientational disorder in compounds containing Jahn-Teller distorted coordination polyhedra", by R.G.J. Strens, Dept. of Mineralogy & Petrology, Cambridge University.

8. "High temperature behavior of inorganic salts with oxyanions", by Kurt H. Stern, U.S. Department of Commerce, National Bureau of Standards, Washington, D.C. 20234.

The lack of a comprehensive, critically reviewed compilation of properties of inorganic salts at high temperatures has stimulated us to prepare such a work.

Compounds are classified according to common anion and the literature is critically reviewed with respect to both qualitative and quantitative behavior. Examples of the former are the intermediate compounds which may form during thermal decomposition and their stability ranges, and the decomposition reactions. Quantitative data included are the thermodynamic functions of the reactions (free energy functions, equilibrium constants, and partial pressures of product gases) at 100° intervals, phase transitions, densities, and chemical kinetic data.

Friday, 15 July

a.m. Session on Kinetic Studies: Thermal Decomposition of Carbonates, Oxalates, etc.

1. "Kinetics of the reaction of water vapor with crystalline lithium hydride", by W.D. Machin and F.C. Tompkins, Chemistry Dept., Imperial College of Science and Technology, London, S.W.7.

The kinetics of the reaction of water vapor with crystalline lithium hydride to produce hydrogen, and either lithium oxide or hydroxide, has been investigated over the temperature range 0-121°C, using samples of hydride of various particle sizes. The chemical nature of the solid product is determined by solely the amount of water vapor added in any single dose; when this is only sufficient to react with a single surface layer of lithium hydride or less, the oxide is formed almost exclusively but when there is sufficient water to react with several layers, only the hydroxide is formed. These conclusions are valid irrespective of the amount or nature of the product present on the hydride from preceding runs. On introduction, water vapor is rapidly and almost completely removed from the gas phase by the solid hydride (and products) but the hydrogen-producing process continues for several hours by reaction of sorbed water with the hydride. Diffusion of sorbed water to the reaction interface is not rate-controlling.

The kinetics of hydrogen production, irrespective of the chemical nature of the product is adequately represented by a first-order process that is retarded by the products of reaction, viz., $\frac{1}{t} \log \left(\frac{a}{a-x}\right) - \frac{Cx}{t} = D$. The parameters C,D are constant during any run but vary with temperature, and

decrease independently as the product accumulates. To account for this latter variation, it is suggested that annealing and recrystallization processes occur in the oxide layers in the time interval between successive additions of water vapor; these structural changes affect the adsorptive capacity of the layers for water and thereby control both the number of water molecules available for reaction at the reactant/solid interface and their reactivity. A quantitative development of these concepts has been given and values for rate constants and activation energies for the hydrogen-producing reaction, and also some relative heats of adsorption of water by the oxide, have been evaluated. The formation of the hydroxide that takes place when larger doses of water vapor are employed is the result of rapid reaction of unreacted sorbed water with the freshly-formed oxide, which is always the initial product of reaction. Hydroxide formation by reaction of sorbed water with the annealed oxide is much slower than its rate of reaction with the underlying lithium hydride, so that for successive small doses of water the only product is the oxide.

2. "Carbon isotope and stoichiometric effects in the thermal decomposition of manganous oxalate", by Harris Burns, Jr., and Peter E. Yankwich, Noyes Laboratory of Chemistry, University of Illinois, Urbana, Illinois 61803.

Results have been obtained on the carbon intramolecular isotope effects and the ratio of gaseous products as functions of temperature and of method of precipitation for the complete decomposition of two types of manganous oxalate. Type CB was prepared by reaction of aqueous sodium oxalate and manganous chloride; type CD was precipitated from reaction of 95% ethanol solutions of the same. Experimental procedures were essentially as reported earlier: Pure Appl. Chem., 8 , 287 (1964).

3. "The thermal decomposition of oxalates of nickel, cobalt and copper", by D. Broadbent, D. Dollimore and J. Dollimore, Royal College of Advanced Technology, Salford 5, Lancashire.

4. "The kinetics of rehydration of solid manganous formate anhydride", by Ted B. Flanagan and Roger C. Eckhardt, Chemistry Dept., University of Vermont.

5. "The photochemical decomposition of sodium bromate", by P.J. Herley and P.W. Levy, Brookhaven National Laboratory, Upton, New York.

The photolytic decomposition of normal and irradiated $NaBrO_3$ has been investigated as part of a broad radiation-effects study which includes thermal decomposition, color center, and esr measurements on this material.

The decomposition kinetics were studied in a greaseless pyrex constant volume system (~2 liters) using an ionization gauge to measure the pressure. The initial background pressure was ~5 x 10^{-7} mm Hg. and the outgassing rate was of the order of 1 x 10^{-6} mm Hg. $hour^{-1}$. The light source used was a General Electric BH-6 High Pressure Mercury lamp with a broad continuum in the ultra-violet which peaks at 3100A°. A water filter removed

most of the infra-red components. The light intensity was varied by introducing quartz neutral filters into the light path. The $NaBrO_3$ used was obtained from large single crystals (9 cms x 9 cms x 9 cms) grown in this laboratory. The only significant impurity detected spectroscopically was potassium. Single crystals were ground to pass through a 53μ mesh sieve. 200 mg samples were used for each run.

At the start of each run the samples were exposed to ultra-violet light and pumped on for sixty minutes to remove surface contaminents. The system was then closed and the pressure continuously measured until it reached one micron. The light was then deflected from the sample, the gas pumped out and the process repeated until reproducible decomposition rates were obtained.

The rate decreased initially and eventually, after a period of several hours, tends to approach a constant value.

6. "Micrographic and microgravimetric study of the decomposition of single crystals of calcite", by G.D. Renshaw and J.M. Thomas, Chemistry Dept., University College of North Wales, Bangor, Wales.

7. "Crystal transformations in the calcining and milling of some calcareous materials", by D.R. Glasson, Chemistry Laboratory, College of Technology, Plymouth, Devon, England.

The paper surveys changes in specific surface, phase composition and crystallite size during calcination <u>in vacuo</u> or in air at a series of temperatures for different lengths of time. These changes can be correlated with the kinetics of the thermal decompositions, which are of type: Solid I $\longrightarrow$ Solid II + Gas. Similar variations in surface properties and crystallite size are investigated during milling processes, where crystal transformations are compared with those produced thermally.

p.m. Session on Experimental Techniques, Thermal Decomposition of Perchlorates and Oxysalts.

1. "A microcinematographic study of the influence of impurities and lattice imperfections on the oxidation of graphite monocrystals", by J.M. Thomas, Chemistry Dept., University College of North Wales, and P.L. Walker, Dept. of Fuel Science, Pennsylvania State University, Penna., 16802

We have endeavored to elucidate the mechanism of the oxidation of carbon by combusting large crystals of natural graphite in the hot-stage of a microscope to which was attached a 16 mm. cine camera. It has proved possible to observe directly several new features relating to the reaction mechanism and to confirm others that have been postulated previously.

With highly purified crystals, in the absence of added solid impurity, it was found that carbon atoms situated at certain types of lattice imperfections (e.g. twin boundaries and bend planes) are not attacked preferentially by oxygen, whereas others are (e.g. atoms in the vicinity of <u>c</u>-axis

screw and edge dislocations.) Moreover, quantitative estimates could be made of the anisotropy of oxidation rates among the <0001>, <10$\bar{1}$0> and <11$\bar{2}$0>directions.

Several unexpected results were obtained when the oxidation took place in the presence of added impurities. Some of the impurities, notably Mo and B, which became molten owing to the formation of oxide, generally facilitated attack by oxygen of lattice imperfections such as twin bands and low-angle grain boundaries. Others, such as Ag, were found to possess a degree of mobility over the {0001} graphite surfaces in excess of that expected from Brownian motion. The technique also revealed that the mobility of small metal particles on a graphite substrate is profoundly influenced by the nature of the gaseous environment.

Other features observable by this technique were: (1) the aggregation and loss of activity of catalyst particles during the course of oxidation; (2) the anisotropic influence of some solid catalysts (e.g. Mn); (3) the "unwinding" of a c-axis screw dislocation during oxidation; and (4) the release of some types of lattice strain (such as bent twin bands) by the heat liberated during oxidation.

2. "Techniques for study by X-ray diffraction of transient and other processes at thermal transformations in crystals", by S.W. Kennedy, University of Adelaide, South Australia.

The paper describes experimental techniques for the study by X-ray diffraction of transformation and subsequent relaxation processes in crystals. Because of their short duration the investigation of these processes requires rapid recording and preferably direct observation of the diffraction pattern. These have been achieved by use of electronic image intensification with a special X-ray goniometer. Exposure times for photographic recording range between 0.2 and 5 sec. and a crystal of a product phase can be brought by inspection to the position for Bragg reflexion without previous precise knowledge of the diffraction angle.

The technique has been used to study the plastic deformation and relaxation which occur during and after transformations. These are expected to be important in the kinetics and thermodynamics of some types of change, yet little information has been available on the rate at which stresses are released. Direct observation of the diffraction pattern showed at transformations in $RbNO_3$ and NH_4NO_3 the new phase is initially highly strained or disordered and the pattern corresponding to a less strained specimen appears gradually over a period of one minute. It is this second pattern which would be recorded by conventional X-ray photography. After the transformation at -16°C in NH_4I, the crystal continued to anneal noticeably for 40 minutes, the rate being initially rapid. The increase in annealing rate with increase in temperature was followed by observing the diffraction pattern. The method has also been used to monitor and control the growth of small $RbNO_3$ crystals from the melt, and to study the space group of a high temperature phase unstable in X-rays.

Another factor involved in the mechanism of structure changes is the amount of misregister at the interface when there is an orientation relation. Discrete change of spacing may be associated with anomalous expansion. It is often difficult to decide from dilatometric measurements whether there is an anomaly or not. These changes have been studied by a precision method employing a narrow but deep crystal-monochromatized X-ray beam incident upon a crystal held in a temperature gradient. This records spacings and changes in spacings on both sides of the interface.

3. "An apparatus for direct measurement of rate of gas evolution in thermal decompositions of solids", by R.A.W. Hill and B.W. Rodger, Imperial Chemical Industries, Ltd., Nobel Division, Stevenston, Ayrshire, Scotland.

Progress in the study of the kinetics of thermal decompositions of solids now depends on more detailed observation of what have proved to be rather complex processes. There is scope for greater experimental accuracy and better methods of kinetic analysis. One possibility is to measure rates of reaction, rather than extents of reaction, and to test theoretical rate equations in their original differential form. In this way more accurate procedures which avoid unknown constants of integration may be devised. In a recent work on potassium permanganate, in which these methods were applied, we used rate measuring apparatus operating at atmospheric pressure. In the present note we describe apparatus similar in principle for carrying out decompositions in vacuum. Both operate by measuring the time required for a fixed quantity of gas to be evolved.

The vacuum system is very simple, consisting of a tube carrying two Pirani gauge heads and two detachable reaction vessels either of which can be heated by means of a bath of molten metal regulated at the required reaction temperature. This part of the apparatus, which has a working volume of about 30 ml, is evacuated through a motor-driven tap, the open and closed positions of which are defined by microswitches. One Pirani gauge-head monitors the pressure on a meter; the other actuates the tap motor through a galvanometer-photocell type relay causing the apparatus to be evacuated when an upper pressure limit has been reached. The tap closes again at a suitable lower pressure limit and the cycle repeats itself as long as the reaction continues.

4. "Controlled atmosphere microscopy; characterization of a hygroscopic perchlorate", by Joseph P. Crisler, U.S. Naval Propellant Plant, Indian Head, Maryland.

5. "The thermal stability and some physical properties of silver chlorite, chlorate and perchlorate", by F. Solymosi, Institute of Inorganic and Analytical Chemistry, Jozsef Attila University, P.O. Box 440, Szeged, Hungary.

Kinetic investigations on the following substances were carried out in the usual vacuum apparatus. Results and proposed mechanisms were reported.

$NaClO_2$	$NaClO_3$	$NaClO_4$
$Ba(ClO_2)_2$	$Ba(ClO_3)_2$	$Ba(ClO_4)_2$
$AgClO_2$	$AgClO_3$	$AgClO_4$
$Pb(ClO_2)_2$	$Pb(ClO_3)_2$	$Pb(ClO_4)_2$

$TlClO_2$ was found to be too unstable to work with.

Order of stability: $ClO_4 > ClO_3 > ClO_2$

$Na > Ba > Ag > Pb$

6. "The thermal decomposition of nickel hexammine perchlorate", by R.A.F. Sherriff and A.K. Galwey, Chemistry Dept., Queen's University of Belfast, David Keir Building Stranmillis Road, Belfast 9, N. Ireland.

7. "The influence of various oxides and physical factors on the thermal decomposition of perchlorates", by A. Burcat, A. Glasner, I. Pelly, I. Shidlovsky and M. Steinberg, the Hebrew University, Jerusalem, Israel.

The thermal decomposition of several perchlorates was investigated.

a. Lithium perchlorate trihydrate (LP). The effect of various transition metal oxides and lanthanide oxides was surveyed. Most of these oxides slightly lowered the decomposition temperature of the perchlorate. NiO was more effective than many other oxides, but the lithium doped oxide inhibited the catalytic action. Zinc oxide, both doped and undoped, had no effect whatever on the temperature of decomposition.

Co_2O_3, Cr_2O_3 and CrO_3 proved the most effective of all the oxides used in this study. Cr(III) is oxidized to the hexavalent oxidation state, but shows no reaction below 285°C; evolution of oxygen begins at a higher temperature after the commencement of the oxidation to the hexavalent state. Addition of CrO_3 had a very significant effect on the reaction temperature and kinetics, hence it may be concluded that the initial production of hexavalent chromium is a decisive factor in the decomposition of LP. Chlorine is liberated in this reaction, and its amount increases proportionately to the relative amount of Cr_2O_3 added to the reaction mixture. The rate of decomposition of LP increased with the molar ratio $Cr_2O_3/LiCl_4$. There is substantial evidence that Cr_2O_3 is oxidized by LP to the hexavalent stage in the condensed (liquid or solid) state. The reaction between $LiClO_4$ vapor and solid Cr_2O_3 was very slow, and the ambient pressure of oxygen did not effect the reaction.

b. Nitrosyl and nitroxyl perchlorates. The kinetics in vacuum were studied by following the pressure increase of the oxygen evolved through the thermal decomposition in the temperature range 90° - 140°C. The induction period with nitrosyl perchlorate was more prolonged than that of pressed discs (25,000 pounds total pressure). Some transition metal oxides and La_2O_3 reacted with nitrosyl and nitroxyl perchlorates to form stable intermediary

perchlorates. Cr_2O_3 catalyzed the reaction without forming an intermediary perchlorate.

c. Lanthanide perchlorates. The effect of water of crystallization on the rate of decomposition of crystal hydrates of praseodymium, neodymium and samarium perchlorates was demonstrated. The decomposition rate was evaluated gasometrically, and the acceleration rate constants of the several lanthanide perchlorates were compared at similar temperatures.

Correlation between the water content of the crystals and the decomposition rate constants was noted. Apparently the number of the decomposition nuclei formed as a result of the evaporation of the water molecules increases with the amount of water originally present in the crystals.

8. "Thermal decomposition of magnesium, silver and samarium chromates", by R.G. Darrie and W.P. Doyle, Chemistry Dept., University of Edinburgh, Scotland.

The thermal decomposition of the chromates of a representative element, magnesium, a transition element, silver, and an inner transition element, samarium, has been studied by thermogravimetry, differential thermal analysis, X-ray powder diffraction, magnetic susceptibility measurements, ultraviolet reflectance spectroscopy and infrared spectroscopy.

From a previous thermogravimetric study of the decomposition of anhydrous magnesium chromate it was concluded that the reaction was first order with an activation energy of 96 kcal. $mole^{-1}$. Silver chromate is reported to decompose only above 812°C with formation of the chromite, silver and oxygen; no previous work on the decomposition of samarium chromate has been reported.

Preliminary DTA and TGA studies showed that magnesium chromate pentahydrate loses three molecules of water at about 215°C, a fourth molecule at about 315°C and the last molecule at about 385°C; decomposition of the anhydrous chromate, to the chromite with loss of oxygen, begins at about 600°C and is complete at about 800°C. The kinetics of the isothermal decomposition of anhydrous magnesium chromate at 600, 610, 623, 635 and 650°C were studied thermogravimetrically. The results agree with those previously reported but the decomposition is not first order; the data can be divided into two stages each of which fits the equation $\alpha = c(t-t')^n$, n less than 1; the activation energies for the first and second stages are 30 and 57 kcal. $mole^{-1}$ respectively. For all partially decomposed samples, all lines in the X-ray diffraction patterns and all features in the infrared and ultraviolet spectra could be assigned to magnesium chromate and magnesium chromite. From the magnetic susceptibilities of the partially decomposed samples and the susceptibilities of magnesium chromate and chromite, the percentage decomposition was calculated and found to be the same as that determined from the observed weight loss.

Preliminary DTA and TGA studies showed that decomposition of anhydrous silver chromate becomes significant about 650°C and is complete at about 870°C. DTA also showed an endotherm at about 480°C which may be due to transition from the red to the green form of silver chromate. The kinetics

of the isothermal decompositon of silver chromate at 600, 610, 620 and 640°C were studied thermogravimetrically. The decomposition can be conveniently divided into three stages the data for each of which fit the Prout-Tompkins equation $\log_{10} [\alpha/(1-\alpha)] = kt + \text{const}$. The activation energy for the main stage of decomposition is 54 kcal. $mole^{-1}$. For the partially decomposed samples, all lines in the X-ray diffraction patterns could be assigned to silver chromate, silver chromite and silver; as for magnesium chromate, the percentage decomposition calculated from measurements of magnetic susceptibility was the same as that determined from the observed weight loss.

For both La and Mg chromates, the activation energy for thermal decomposition is very nearly equal to the energy of the first charge transfer band in the electronic absorption spectra of the two substances.