Journal of Thermal Analysis, Vol. 5 (1973) 483–497

STUDY OF CRYSTAL TRANSFORMATIONS BY AN EVOLVED GAS ANALYSIS TECHNIQUE

P. D. GARN and R. L. TUCKER*

*The University of Akron, Akron, Ohio; *Goodyear Tire and Rubber Co., Akron, Ohio, U.S.A.*

(Received March 27, 1972)

Small organic molecules can be entrapped within inorganic crystalline materials during precipitation. The material has no apparent influence on solid-solid transition temperatures, but some of it is released during the transition.

Detection of the escape is reproducible within 1°C and may be used for temperature calibration. More generally, the escape of the organic during chemical reactions could be used for many of the applications of emanation thermal analysis.

In coupled systems such as DTA or TG with mass spectrometry, or other systems involving gas transport, the time delay of the system can be measured accurately.

Gases released by chemical reaction or radiochemical decay of solids do not always escape quickly from the solid. They may remain well dispersed in a well-formed lattice or collect at grain boundaries or form discrete pockets, depending upon the mobility through the solid. The release of these gases may be easily accomplished by fusion of the solid if analysis of the gas is the objective, as in the well-known case of radioactive dating. On the other hand, partial release may be effected by less drastic changes of state or by chemical dissolution of the solid.

Release of gas during fusion has been suggested for use as a temperature calibration of evolved gas analysis. Ware [1] dissolved CO_2 in molten K_2SO_4 and found (within a batch) good reproducibility in the temperature at which gas evolution was detected. He found, for one batch, a temperature of 1061.4 ± 2.0°C for the initial gas evolution. One possible contribution to the variation is the probable non-homogeneity of temperature in the 100 mg sample.

The study of crystallographic phase changes by measurement of radioactive emanation from a gas escaping from within the grain boundaries of various compounds has been used by analysts applying the Emanation Thermal Analysis technique. The procedure involves the detection of radioactive inert gases that had been entrapped within the crystal lattice of various solids, and are evolved from the solid discontinuously as the solid passes through a change of state. The present work describes a method having many of the capabilities of emanation thermal analysis with the important advantage of ease of preparation and greater latitude in means of detection.

During emanation analysis, a linear temperature increase is applied to the sample while the sample chamber is swept continually by an inert carrier gas. At the temperature of transformation, the enriched concentration of radioactive gas, relative to the carrier gas, is sensed by the counter.

Bussiere and Claudel [2] reported the use of this technique in studying the thermal decomposition of thorium nitrate hydrate and thorium oxalate hydrate. Fouilloux et al. [3] studied the crystallographic changes of manganese oxide by an emanation method. Balek [4] describes numerous other applications using emanation techniques.

This present technique can perform some of these same functions plus some others. In this technique, small organic molecules are entrapped within the grain boundaries of the solid material by rapid precipitation from a partially aqueous solution. During the transitory disorder accompanying a phase transformation some of the solvent escapes as a gas and may be detected by any appropriate method. In this work a flame ionization detector was used because of its sensitivity and availability.

The technique makes use of the decreased solubility of many inorganic materials in water-organic mixtures as compared to water. The chosen organic is added quickly to a stirred near-saturated aqueous solution of the inorganic. A large fraction of the inorganic comes out of solution rapidly enough to entrap a small amount of the organic "indicator". The evaluation was carried out in a cell constructed for the purpose.

Experimental

Apparatus

The salt transition cell is shown in Fig. 1. All the metal components are type 316 stainless steel. The body of the cell is 5.08 cm in diameter and 10.10 cm long. The cap is 6.65 cm in diameter and 4.40 cm long. One piece of 0.635 cm diameter bar was used for physical support, fitting into the second detector inlet fitting. The inlet tube is 0.318 cm O.D. and the outlet is 0.635 cm O.D. to fit the connection to the detector cell of the gas chromatograph (F8M Model 810). A tee on the inlet tube permitted introduction of a control thermocouple. The cavity was sealed using a Flexitallic gasket, Model R1-64, made of Type 304 stainless steel with asbestos filler.

An F&M Model 810 chromatograph equipped with flame ionization detectors was modified somewhat for this work. The columns were removed and a direct gas connection made to the transition cell. The control thermocouple in the transition cell was connected to the chromatograph temperature control circuit. The heaters in and around the cell were supplied from that circuit.

For most work, two cartridge heaters (Hewlett-Packard Model 3601), inserted into the body of the transition cell, supplied enough heat. For higher temperatures, up to 680°, a 400 watt cylindrical heating element, ceramic with Kanthal winding, was placed around the cell and wrapped with asbestos. This heater was supplied directly from a variable autotransformer. The ceramic heater was not programmed. The output from the electrometer circuit was taken directly to external circuitry.

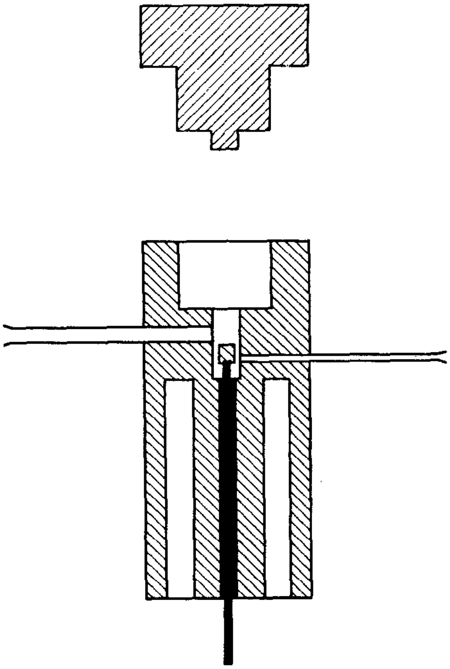

Fig. 1. Sample holder for detection of evolved gas

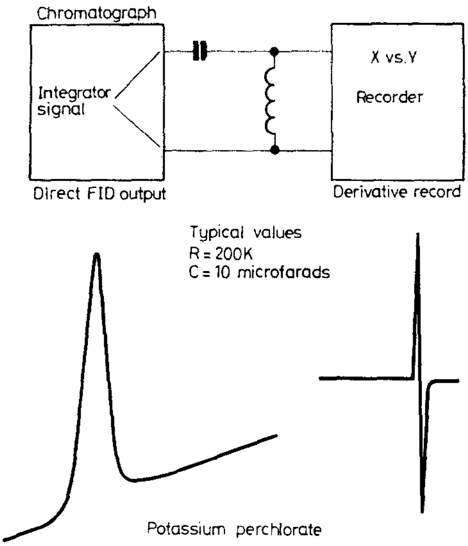

Fig. 2. Recording circuitry and typical signals

The measuring thermocouple, Conax (K–SSG–G–PJ–12), entered the transition cell from the bottom and supported the cup into which the specimen was placed. This provided good measurement of the specimen temperature and a means of physical separation from the block. The leads were taken to an ice bath, where connection to copper was made. A thermocouple potentiometer was used to offset the signal quantitatively, allowing use of the 10 mV range of the external recorder. This was a Houston Model 97 X–Y recorder. The second input signal was either the output from the electrometer or the first derivative of the output.

For samples showing a high rate of escape of the indicator, a derivative circuit (Fig. 2) was inserted between the electrometer output and the recorder. This provides sensitive detection of change even with a relatively high "background" signal.

Reagents

For the evaluation of the technique, reagent grade chemicals similar to those used in the standardization program of the International Confederation for Thermal Analysis [5] were used. These had been examined very thoroughly for their behaviour in differential thermal analysis. Selected batches of some of these materials have been issued by the United States National Bureau of Standards as parts of Standard Reference Materials 758–9–60 [6]. The materials tested in this work were potassium nitrate, perchlorate, bisulfate, chromate, sulfate, carbonate and sodium carbonate.

The solvents used to provide indicators were reagent grade methanol, 2-propanol, 1-propanol, 1,4-dioxane and absolute ethanol.

Procedure

A 100 ml portion of distilled water was saturated with the salt being tested and stirred while 400 ml of the indicator solvent were poured rapidly into the water solution. Precipitation of the salt occurred immediately. The salt was filtered from the solution and dried by aspiration of the filter paper for thirty minutes. Additional drying was performed by oven conditioning of the salt at 100° for known lengths of time. The salt was then immediately placed into a glass vial, sealed and labelled according to salt, indicator and conditioning.

The analysis parameters were held constant except for sample size and temperature limits. The following instrumental conditions were used:

Temperature program rate	4°/min
Helium flow rate through cell	30 ml/min at 10 PSIG
Air flow rate	375 ml/min at 26 PSIG
Hydrogen flow rate	30 ml/min at 10 PSIG
Detector temperature	150°
Detection mode	dual flame

Two blanks were run, the cell with empty sample cup then with the salt as taken from the manufacturer's bottle. This established the absence of possible previous impurities entrapped within the grain boundaries. A single run was made, at a test sample size, on a salt precipitated with indicator solvent. This determined whether entrapment had occurred on precipitation and established a flame ionization response for a known sample size. This led to sample sizes, depending on the salt, from approximately 6 to 30 mg.

Nine determinations were made on each salt to determine the reproducibility of each crystal lattice transformation temperature.

Results and discussion

Potassium nitrate was investigated first, using alcohols as indicators. The transition temperature for potassium nitrate going from orthorhombic to rhombohedral configuration is 128° [7]. All the alcohols, methanol, ethanol, 1-propanol and 2-propanol, showed similar behaviour. Intermittent evolution of alcohols occurred during testing which led to multiple peaks as detected by the flame ionization detector. Similar behaviour can be detected by DTA even without organic indicators [8]. These peaks seemed to occur in clusters around the 128° transition temperature. A recurring peak spanned a 114° to 118° temperature range. Intensity of the responses and reproducibility of the peaks in regard to

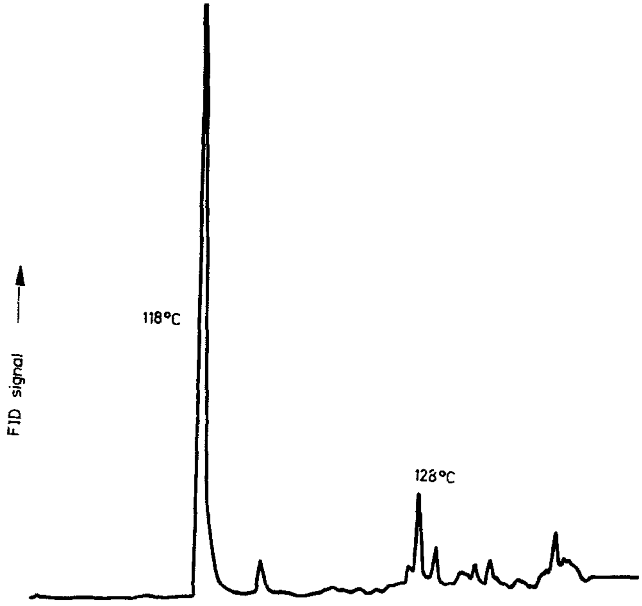

Fig. 3. Ethanol-treated potassium nitrate

temperature was poor. Figure 3 is a typical determination on potassium nitrate using ethanol as the indicator. With alcohols, normal behaviour at the transformation temperature did not occur for potassium nitrate. "Normal" behaviour is defined as a single smoothly-varying peak at or near the thermodynamic transition temperature.

Dioxane-1,4 was also used to precipitate potassium nitrate. The salt was conditioned at 100° for two hours. With 1,4-dioxane as indicator, a "normal" pattern

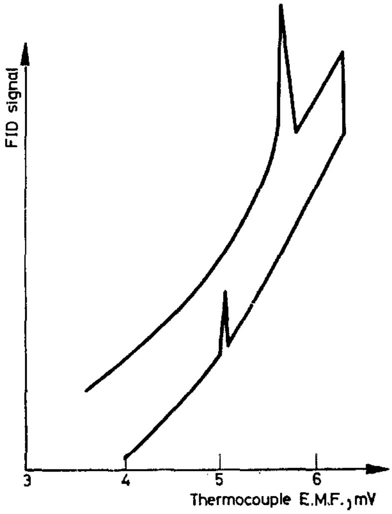

Fig. 4. Dioxane-treated potassium nitrate. See Table 1

Table 1

Potassium nitrate
Indicator solvent: 1,4-dioxane, conditioned 2 hours at 100°

Determination	Sample weight, mg	Departure point, mV	Peak value, mV
1	34.5	5.35	5.48
2	30.7	5.40	5.53
3	25.2	5.39	5.52
4	23.9	5.39	5.51
5	37.7	5.38	5.52
6	28.9	5.38	5.50
7	25.9	5.37	5.49
8	25.4	5.35	5.50
9	26.3	5.35	5.51
Average values	28.7 mg	5.37 mV	5.51 mV
Standard deviation (σ)		0.02 mV	0.02 mV
Average temperature		131°	134.5°

on heating occurred with evolution of the gas at approximately 131°. The peak seen at 131° is ragged, hinting that multiple emission of entrapped gas from individual particles is still occurring – not necessarily simultaneously or uniformly. Table 1 shows the individual determinations made on potassium nitrate along with the absolute standard deviation. Figure 4 is a representative X–Y trace on this salt. Direct mV response was used from the flame ionization detector electrometer. A cooling curve is also shown in Fig. 4. It should be noted that an evolution of indicator occurs on cooling at 122° as the salt transforms to the lower temperature configuration. As in DTA, a cooling cycle can be monitored by this method.

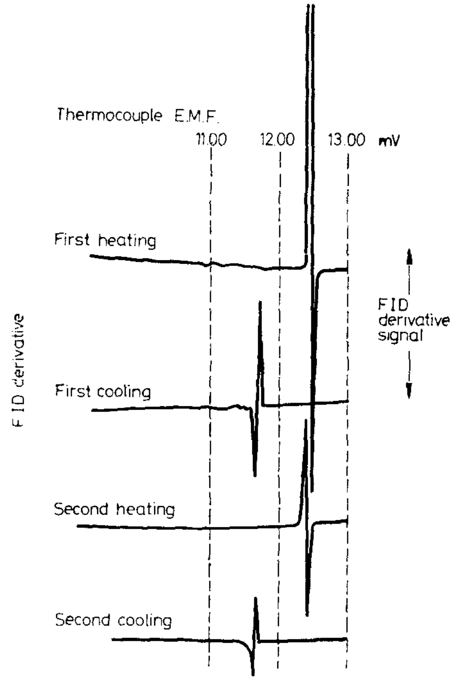

Fig. 5. Ethanol-treated potassium perchlorate. See Table 2

Potassium perchlorate was precipitated with ethanol. Ethanol was entrapped and was emitted at the transition temperature of 300° as the salt went from the orthorhombic to the cubic configuration [9]. Conditioning of this salt was conducted for 12 hours at 200°. The signal from the detector was strong enough to permit the use of a derivative circuit. Figure 5 is a representative analysis on potassium perchlorate showing a heating curve, a cooling curve and a second cycling of the same sample. Less indicator is sensed on subsequent reheating of the sample. After transformation, the new configuration entraps migrating indicator molecules

Table 2

Potassium perchlorate
Indicator solvent: ethanol, conditioned 12 hours at 200°

Determination	Sample weight, mg	Peak value, mV
1	6.9	12.40
2	5.1	12.45
3	6.3	12.39
4	5.2	12.43
5	4.9	12.36
6	7.5	12.41
7	5.6	12.36
8	7.2	12.38
9	5.1	12.42
Average values	6.0 mg	12.40 mV
Standard deviation (σ)		0.03 mV
Average temperature		304.5°

that were held in crevices distant from the surface. Eventually, through multiple transitions, the sample would bleed itself of all indicator molecules. Table 2 contains the results for potassium perchlorate along with the precision obtained.

Potassium bisulfate gave no indication of entrapment of methanol or ethanol. Propanol-2 was entrapped but gave weak indication of peaks and appeared to

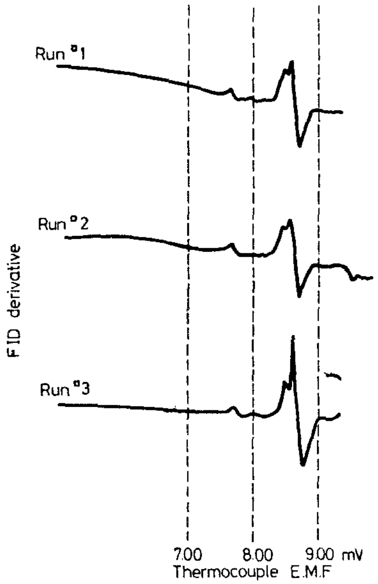

Fig. 6. Dioxane-treated potassium bisulfate. See Table 3

ose indicator at room temperature on aging. Dioxane-1,4 was found to give the best response as well as good aging properties. Conditioning was performed for 30 minutes at 100°. A derivative conversion of the detector was used on this salt. Figure 6 shows three potassium bisulfate runs using 1,4-dioxane as indicator. Four events were measured. The first at 167° was poorly defined and can best be seen on run # 2 as an inflection of the baseline at 6.81 mV. The second event occurs at 190° and is a known crystal transformation observed by DTA analysis

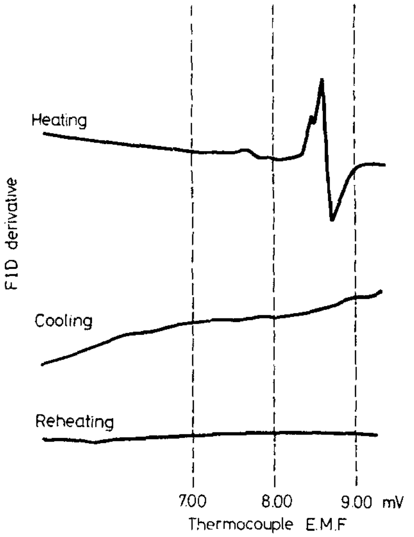

Fig. 7. Dioxane-treated potassium bisulfate, cycled

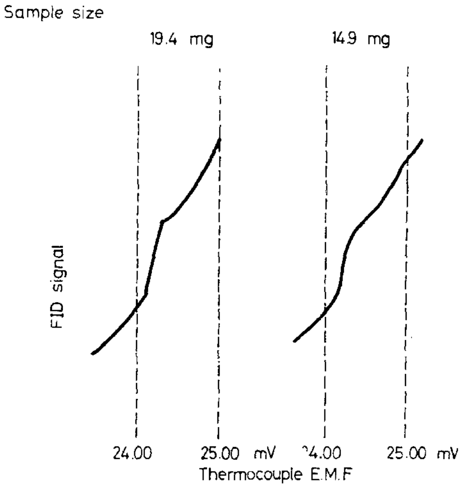

Fig. 8. Dioxane-treated potassium sulfate. See Table 4

at roughly the same temperature. The last two events are not caused by solid to solid transformation but are due to solid → liquid phase change. The melting point of potassium bisulfate is given as 210° [10]. Two events are observed on melting, the first is an evolution of gas as the lattice weakens on melting and the second is the release of the indicator from the melted potassium bisulfate. Table 3 contains the results for nine determinations on this salt. Figure 7 is a run on potassium bisulfate showing a heating, a cooling and reheating cycle. Once melting has occurred, no retention of indicator within the grain boundaries is observed; no cooling events are seen and there is no evolution of gas on reheating. Only solid → solid transitions permit the observance of cooling events.

Table 3

Potassium bisulfate
Indicator solvent: 1,4-dioxane, conditioned 30 minutes at 100°

Determination	Sample weight, mg	Peak value # 1	Peak value # 2	Peak value # 3	Peak value # 4
1	9.2	—	7.73	8.52	8.63
2	8.9	6.70	7.72	8.47	8.61
3	13.9	6.80	7.74	8.50	8.68
4	9.4	6.83	7.78	8.52	8.67
5	10.0	6.88	7.73	8.51	8.66
6	11.5	6.73	7.73	8.51	8.64
7	11.4	6.78	7.75	8.53	8.67
8	12.9	6.87	7.72	8.52	8.65
9	10.5	6.87	7.74	8.53	8.66
Average values	10.8 mg	6.81 mV	7.74 mV	8.51 mV	8.65 mV
Standard deviation (σ)		0.06 mV	0.02 mV	0.02 mV	0.02 mV
Average temperatures		167°	190°	209°	213°

Potassium sulfate undergoes a lattice transformation from the orthorhombic to hexagonal configuration at 583° [11]. Alcohols did not indicate transition at this temperature. Dioxane-1,4 was evolved from this salt with a weak signal that was used directly without conversion to the derivative. Figure 8 shows duplicate determinations for potassium sulfate. Table 4 contains the data for this salt along with the precision obtained. Figure 9 is an analysis on this salt showing a heating, a cooling and a reheating cycle. This figure indicates a cooling event at 581° along with evolution of the indicator on reheating. This salt exhibits normal behaviour for solid → solid transformation.

Potassium chromate undergoes a crystallographic phase change from orthorhombic to hexagonal at 663° [12]. This salt gave no indication of emission of the alcohols or 1,4-dioxane at transition temperature. It is possible that indicators of this size diffuse readily from the grain boundaries at elevated temperatures.

Table 4

Potassium sulfate
Indicator solvent: 1,4-dioxane conditioned 4 hours at 100°

Determination	Sample weight, mg	Departure point, mV	Peak value, mV
1	20.2	24.08	24.35
2	16.0	24.09	24.30
3	19.8	24.10	24.36
4	14.9	24.12	24.38
5	15.7	24.16	24.37
6	19.4	24.08	24.32
7	16.1	24.10	24.30
8	16.2	24.10	24.30
9	17.0	24.11	24.34
Average values	17.3 mg	24.10 mV	24.34 mV
Standard deviation (σ)		0.03	0.03 mV
Average temperature		581.0°	586.6°

Chemical reaction between the indicator and the salt could also occur. A selection of a higher boiling, less reactive indicator may permit use of the potassium chromate transition by this technique.

The carbonates, both potassium and sodium, did not precipitate satisfactorily because of their affinities for water, leading to hydrate formation on precipitation

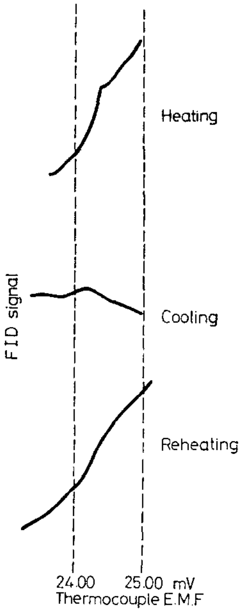

Fig. 9. Dioxane-treated potassium sulfate, cycled

with methanol or ethanol. The other solvents would not initiate precipitation. During analysis, excessive noise and baseline drift was seen on the gas chromatographic recorder. After analysis, the cell cavity indicated spattering of sample, probably caused by boiling of the water of hydration.

In separate experiments, the weight loss of potassium perchlorate on first heating was about 0.3% for one batch [13] and about 0.10% for another [14].

DTA curves for the several materials showed no shifts of transition temperature of the treated samples as compared to the reagent grade materials.

The gas evolved from potassium bisulfate yielded the same mass spectrometry patterns as the dioxane itself, so there is no evidence of chemical reaction. The process can be assumed to be purely physical.

Discussion

The indicator molecules appear to be trapped specifically along grain boundaries rather than being incorporated into the lattice or adsorbed on surfaces. If the indicator was on the surface and strongly-enough adsorbed that it was retained through the conditioning period, it would be unlikely to desorb discontinuously upon heating through a phase transition *and* upon cooling through that phase transition *and* upon reheating and recooling.

Further, the indicator is not trapped within the lattice because the strain upon the lattice would tend to shift the transition temperature and/or distort the DTA peak shape. Neither event was observed, even with apparatus capable of detecting changes of transition temperature of 0.1 – 0.2° without difficulty, and spreading out a peak so that anomalies may be easily seen.

The evidence indicates that the indicator is collected in the disordered regions between grains of well-crystallized materials, and that during the physical movement accompanying a transition the indicator, substantially above its boiling point, is able to diffuse more rapidly and some escapes. Upon reestablishment of rigidity of the grains, the pathways are closed – or at least no new ones are opened. Cooling through the transition has much the same effect; there is a short-lived opportunity to diffuse through or out of the particle. Whether or not this increase in escape is due to opening of new pores or opening and closing of the same paths with migration from deeper within the particle is not answered definitively by these experiments. It could be answered by measurements of the escaping gas for protracted periods without taking the material through the transition, then taking it through the transition and again following the decreasing escape. More important, though, is the recognition that the technique exists and may be put to use.

In general, the technique may be used wherever there is a need to detect when a temperature has been reached but actual measurement is impracticable. An obvious case is temperature calibration of systems such that a thermocouple cannot be placed in the sample, for example thermobalances in which no direct connection is made to the sample holder. A possible use is checking of programmed temperature chromatographs for uniformity of temperature. Incorporation of six to twenty weighed granules of treated potassium perchlorate, for example, at various points in the packing would enable the user to determine whether or not the column was being heated uniformly. If separate peaks are seen, the positions from which they come could be determined by the sizes of the peaks and the known weights of the particles.

Another use, suggested by Mackenzie [15], would be to measure the time delay in systems which involve gas transport. For example, the coupling of mass spectrometers and filters to other devices is highly informative, but if the transit time from the sample to the spectrometer is known, still more information could be extracted from many experiments.

For these uses it must be noted that no measurement has been made of the water which must also be trapped within the particles. The flame ionization detector does not respond noticeably to water, so these may well be a sizeable fraction of water in the escaping gas. Experiments to check this are planned.

Balek [4] has summarized a number of radioactive kryptonated indicators used in volumetric analysis. In general, the titrant reacts with the substance being determined until the latter is exhausted, then with the indicator. At this point an increase in radioactivity is detected by the Geiger-Müller counter. Similar detecting systems are reasonable using treated salts, carbonates or oxides and an appropriate detector. The salts included in this initial survey would not necessarily be useful, but production of treated silver salts as detectors for CN^- or EDTA should not be difficult. Treatment of other carbonates by precipitation from quasi-aqueous solutions should also be feasible so that titration with strong acids is detectable. These methods, of course, do not depend upon release by heating but by chemical attack upon the indicator solid.

Conclusions

The incorporation of organic molecules within the grain boundaries of many solids can be accomplished without difficulty. The escape of these molecules can be used to indicate the occurrence of a change of state.

The escape of indicator molecules during phase transformations may be used for temperature calibration or for measurement of time lags in apparatus.

The escape of indicator molecules during dissolution of the solid host should be useable for end-point detection in volumetric measurements (of highly colored solutions, for example).

The method can be used for many, but not all, of the applications of emanation analysis. On the other hand, the indicators are easily prepared, no radioactivity hazard exists, and the equipment needed is found in virtually all laboratories.

*

The authors are grateful to the National Science Foundation for support of parts of this work through institutional and research grants and to the Goodyear Tire and Rubber Company for use of the chromatograph and other facilities.

References

1. Robert K. Ware, Thermochim. Acta, 3 (1971) 49.
2. P. Bussiere, B. Claudel et al., J. Chim. Phys., 58 (1961) 668.
3. P. Fouilloux, P. Bussiere and B. Imelik, Compt. Rend., 256 (1963) 3682.
4. V. Balek, Anal. Chem., 42 (1970) 16A.
5. ICTA Committee on Standardization, Evaluation of Potential DTA Standards. Summary Report of Meeting at Northern Polytechnic, Report No. ICTA 67-02, London, Sept. 20–22, 1967.
6. U. S. National Bureau of Standards Circular 238, Superintendent of Documents, U.S.G.P.O., Washington, D.C.
7. W. H. Zachariasen, Skrifter Norske Videnskaps — Akad. Oslo, I: Mat. Naturv. Kl., 10 (1928) 14.
8. P. D. Garn, Anal. Chem. 41 (1969) 447.
9. A. Basche and H. Mark, Z. Krist., 64 (1926) 1.
   H. Bräkken and L. Harang, Z. Krist., 75 (1930) 538.
   K. Herrmann and W. Ilge, Z. Krist., 75 (1930) 41.
10. N. A. Lange, "Handbook of Chemistry", McGraw-Hill, New York, N. Y. 1967, p. 305.
11. W. Ehrenberg and C. Herman, Z. Krist., 70, (1929) 163.
    G. Pannetier and M. Gaultier, Bull. Soc. Chim. France (1966), 188.
12. C. Pistorius, Z. Phys. Chem. (New Series), 35 (1962) 109.
13. George M. Theall, private communication.
14. Hans-Georg Wiedemann, private communication.
15. Robert C. Mackenzie, private communication.

Résumé — De petites molécules organiques peuvent se trouver incluses dans des substances inorganiques cristallines, au moment de la précipitation. Les températures de transition solide-solide ne s'en trouvent apparemment pas affectées mais une partie de ces molécules incluses peut être éliminée pendant la transition. La détection du matériau qui s'échappe est reproductible à 1°C près et se prête à l'étalonnage de la température. En termes plus généraux, le départ de la substance organique au cours des réactions chimiques peut être utilisé pour de nombreuses applications de l'analyse thermique d'émanation. Dans le cas de techniques associées, comme l'ATD ou la TG avec la spectrométrie de masse, ou encore d'autres techniques avec transport de gaz, on peut mesurer exactement le temps de réponse du système.

Zusammenfassung — Kleine organische Moleküle können während der Fällung in anorganische kristalline Substanzen eingeschlossen werden. Die Substanz hat keine scheinbare Wirkung auf Fest-Fest-Übergangstemperaturen, doch wird ein Teil derselben während des Überganges freigesetzt. Der Nachweis der freigesetzten Substanz ist innerhalb von 1°C reproduzierbar und kann zur Temperatureichung eingesetzt werden. Verallgemeinert könnte das Entfliehen organischer Substanzen im Laufe chemischer Reaktionen bei vielen Anwendungen der Emanations-Thermalanalyse eingesetzt werden. In gekoppelten Systemen, wie z.B. DTA oder TG mit Massenspektrometrie, oder andere Systeme mit Gastransport, kann die Verzögerung des Systems genau gemessen werden.

Резюме — При осаждении небольшие органические молекулы могут оказываться включенными в неорганические кристаллические материалы. Они не оказывают явного влияния на температуры перехода твердое—твердое, но некоторое их количество освобождается во время перехода. Их выделение регистрируется с воспроизводимостью в пределах 1°C, что может быть использовано для калибровки температуры. Вообще выделение органики в ходе химических реакций можно использовать для многих случаев применения эманационного термического анализа. В комбинированных системах, таких, как ДТА или ТГ с масс-спектрометром, или в других системах, включающих транспорт газа, задержка времени системы может быть измерена с большой точностью.