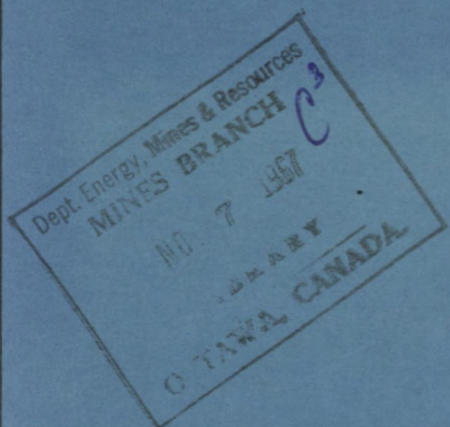




CANADA

DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

*KINETIC AND THERMODYNAMIC
DATA FROM EFFLUENT
GAS ANALYSIS*



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EXTRACTION METALLURGY DIVISION

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Introduction

In 1933 H. A. Daynes wrote, in the introduction to his book on Gas Analysis (1),

"The practicability of the thermal conductivity method has been known for at least twenty years and, in certain applications, notably the control of combustion in steam-raising plants and the control of ammonia synthesis, it is established as suitable for industrial conditions. Yet in some directions its use has been surprisingly limited."

Notwithstanding the detailed analysis of the method provided by Daynes (1), the first major development in the use of thermal conductivity methods was that of James and Martin (2) who published a classical paper in 1952 in which they described the use of a gas-liquid partition technique for resolving aliphatic acids. The biochemical field was ripe for the development of this elegant technique, and since that time thousands of papers have been published on the application of these principles to various analyses.

The combination of thermal conductivity detectors with gas-liquid partition techniques has been very fruitful, but further developments are not limited to the analysis of still more complex gas or liquid mixtures. In this paper, experimental

methods will be described in which the gas-liquid partition column has been replaced by a simple saturation column or a column containing a pelletized sample. These substitutions permit the gathering of thermodynamic and kinetic data on various processes, and the method permits utilization of much of the automation repertoire built up for complex gas sample analysis.

Principles of the Thermal Conductivity Method

The basic idea of the thermal conductivity method is that the temperature attained by an electrically heated wire in a confined space is a function of the conductivity of the gas atmosphere surrounding it (3). The method of applying this principle to the analysis of gas mixtures is illustrated by Fig. 1, which shows a fine tungsten filament suspended in a cavity in a metal block. The block is heated to a constant low temperature and fitted with ports through which the gas mixture to be analyzed is passed at a constant rate of flow. Because the resistance of the filament is proportional to its temperature, which is a function of block temperature, heating current, and the flow rate and conductivity of the gas, it is evident that when wall temperature, heating current and gas flow are kept constant, the filament resistance will be a function of the thermal conductivity of the gas mixture. In gas mixtures, the thermal conductivity of the mixture is a function of its composition. It is evident, then, that the resistance of a filament will vary with the composition of the gas surrounding it. When the filament is made part of a Wheatstone bridge circuit, the off-balance of the bridge is a function of the composition of the gas passing through the cell. With very simple equipment, changes in the off-balance of the bridge may be recorded continuously, and in this way changes in the composition of the gas stream may be monitored effectively.

Geometric considerations within a thermal conductivity cell are too complex to permit an accurate calibration of a cell to be calculated from first principles. However, the cells may be calibrated readily by a variety of well-established techniques (4, 5, 6).

Application to Single Sample Analysis

Fig. 2 shows a typical schematic diagram of the apparatus used for the separation and analysis of the constituents of a complex gas or liquid sample. Two thermal conductivity cells are used in the compensating arms of a Wheatstone bridge circuit. A constant stream (e.g., 50 cc.min.⁻¹) of a high-conductivity, non-reactive gas, such as helium, is passed through one of the cells which acts as a reference. Beyond this cell, the sample is injected into the gas stream. When a low-boiling liquid sample is used, the sample port must be heated to volatilize it. The sample may be introduced with a syringe, or through a series of electrically-activated gas ports.

The sample-carrier gas mixture is then passed into a chromatographic column. In its simplest form this may be a length of capillary tubing moistened with a film of a silicone oil, or it may be a combination of liquid and solid components which adsorb or react with some of the constituents of the sample. In any case, the basic principle is that the column must provide a means for differentially segregating the components of the gas mixture, normally through adsorption to different degrees. Those components that are only slightly adsorbed pass through the column quickly, while those that are strongly adsorbed take part in a slow adsorption-elution cycle which retards their passage through the column. When the sample is introduced quickly as a well-defined "plug", the slightly-adsorbed material is eluted and its passage recorded by the sample side of the thermal conductivity detector in the form of the sharply-defined peak shown on the left of Fig. 3. The more strongly-adsorbed component of the sample is retained longer and eluted more slowly, to produce a more diffuse peak similar to that shown on the right of Fig. 3. To determine the percentage of each component in the mixture, it is only necessary to determine the area under each of the peaks and multiply each by its own calibration factor. For simple systems this factor may be determined by the introduction of a known volume of a pure component with a syringe (4, 5, 6).

Application to Thermodynamics

Only a minor change in design is required to make thermodynamic measurements with the thermal conductivity apparatus shown in Fig. 2. The change consists of substituting a different column for that used to separate the components of a

complex gas mixture. Two typical column designs (7) for making thermodynamic measurements are shown in Fig. 4. The column shown at the top of the figure is used for liquid samples, and that at the bottom for solid samples. Each column is designed to expose a large surface area of either liquid or solid to the carrier gas. Within the general range of carrier gas flow rate from 15 to 50 cc. min.⁻¹, the sample develops in the carrier gas a partial pressure identical to either its vapour pressure or its dissociation pressure. This is the basic principle of the transport or transpiration method (8) of determining vapour pressures or dissociation pressures. When the carrier gas has been equilibrated with the sample in the column and passed into the sample side of the thermal conductivity detector, its response at a variety of temperatures is similar to that sketched in Fig. 5. The time interval for attaining the steady value on the plateau may vary from about one-half hour to several hours.

To resolve the equilibrium vapour pressure or the dissociation pressure of the sample from the data shown in Fig. 5, a calibration curve must be prepared for the system being studied. For example, if one wishes to study the dissociation pressures of some solid hydrates or hydroxides, the solid sample column (Fig. 4) could be used and the apparatus calibrated with distilled water in the liquid sample column (7). The millivolt response versus partial pressure calibration curve is prepared from the data for pure water.

We have used this combination of the thermal conductivity method with the transport method to study the dissociation of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (7), $\text{BaCl}_2 \cdot \text{H}_2\text{O}$ (7), CuO (8), MnO_2 (8), and Mn_3O_4 (8), and find that it has certain advantages over the static method. When the static method is used, both the solid reactant and the solid product are held in a partial pressure of the product gas until equilibrium is attained. The presence of the product gas tends to hasten the attainment of equilibrium. In the transport method, as used in these experiments, the solid product is not maintained in a partial pressure of the product gas but, once formed, is primarily in contact with carrier gas only, as shown in Fig. 6. As a result, if there is any possibility of forming metastable intermediates in the decomposition process, these forms tend to be stabilized by this method of study. Although energy change calculations made from this type of experiment agree well with equilibrium thermodynamic values when intermediate materials are not involved, they may differ by about 5 kcal.mole⁻¹ when intermediates are formed. The method also

has certain advantages for assessing the energy changes in actual metallurgical processes, because the products formed during a transport study will probably be the same as those made during actual metallurgical operations.

Applications to Kinetics

When the gas separation column shown in Fig. 2 is replaced by the type of column shown in Fig. 7, the standard chromatographic apparatus is suitable for making kinetic studies. The sample should be small and of uniform dimensions. It may be cut from a solid lump, or prepared by pressing a pellet from a fine powder. The essential feature is that the sample shape should be chosen so that its volume may be calculated by a simple mathematical expression. This is done to normalize the observed rate of decomposition for the change in interfacial area which is caused by the reaction, the method of making this normalization having been described earlier (9).

For convenience in computer programming of the results, a standard pellet 1/4 inch in diameter by 1/20 inch in height was chosen for the gas kinetics experiments reported in this paper.

The column shown in Fig. 7 can be arranged for experiments with either a constant temperature or a linearly-programmed increasing temperature. When an isothermal program is to be used, the cell is equilibrated with the sample in the cool zone of the column. The reaction is begun by pushing the sample on its platinum mesh holder into the heated reaction zone, where it is suspended over a thermocouple.

Isothermal Experiments

The results from a typical isothermal decomposition experiment are shown in Fig. 8. The area enclosed by the curve is proportional to the size of sample used. The fraction of reaction after 25, 50 and 75 per cent of the reaction period may be calculated from the fractional area enclosed under the curve up to that time. The necessity of normalizing this calculated fraction of reaction will be evident from the shape of the curve, which indicates that proportionately less gas is evolved during the same reaction time at the end of the reaction period than at

the beginning. If there were no change in sample geometry, the cell response curve would tend to follow the dotted rectangular pattern.

The effect of geometry change during decomposition is even more marked in Fig. 9, where both the fractional amount of CO_2 released during the decomposition of CaCO_3 , and its normalized result, are plotted against time. The curve is a combined function of the gas loss and the geometry change. The slope of the straight line is the rate constant for the decomposition reaction. From the uniformity of the slope it is evident that the rate of decomposition is constant at all stages of the reaction.

When the experiment is repeated at various temperatures, the activation energy of the reaction may be calculated from an Arrhenius plot of the logarithm of the rate constant versus reciprocal temperature.

Linearly-Increasing Temperature Experiments

The apparatus shown in Fig. 7 is also used for kinetic experiments in which the activation energy for a decomposition reaction is resolved from a single run using a constant rate of heating. It is necessary, for the interpretation of data, that the heating rate be essentially linear over the temperature range used. It is sufficient to ensure that the emf-time relationship is linear, because the variation in the emf-temperature relationship is within the 1 to 2° control error over the 200°C. interval used in most experiments.

When a 1/4 x 1/20-inch pellet of reagent-grade CaCO_3 was heated in a 50.0 cc. min.^{-1} stream of He at a rate of $1.0^\circ\text{C. min.}^{-1}$, the results shown in Fig. 10 were obtained. Using the basic components given in Table I, one pen of a two-pen recorder traced the linear heating programme, which showed deviations from linearity of less than $\pm 1^\circ\text{C.}$ over a 200°C. range. One of the interesting features of the experiment is the sensitivity of the thermal detectors. When the signal is monitored with an integrating unit in parallel with the recorder, decomposition was detectable at 550°C. when there was about 4 ppm. of CO_2 in the carrier gas. In the absence of an integrating unit, the fraction of decomposition attained after a specific period of time (i.e., up to a specific temperature) may be calculated using the same method of fractional area normalization as for the isothermal experiments.

The method of interpreting the fractional decomposition versus linearly increasing temperature data (6) is applicable both to effluent gas analysis data and to data obtained by thermogravimetric methods. The following rigorous development supercedes earlier suggestions (10).

In terms of the Eyring theory of absolute reaction rates, the number of moles, n , of material liberated from unit interfacial area in unit time is:

$$dn/dt = AkT/\lambda^2 h \exp(-\Delta H^\ddagger/RT) \exp(\Delta S^\ddagger/R), \quad [1]$$

where A is the interfacial area, λ the distance required to liberate the product gas from the lattice, and k , T , h , ΔH^\ddagger , ΔS^\ddagger and R have their usual designations.

To normalize the expression for application to a group of samples of different weights, the fraction of reaction, α , at time t , is represented as n/N , where N is the total number of moles of gas liberated at the completion of reaction:

$$\alpha = n/N, \quad d\alpha = dn/N. \quad [2]$$

Also, since a linear temperature program is used,

$$T = at + C \quad \text{and} \quad dT = a dt, \quad [3]$$

where a is the rate of temperature increase in degrees per minute and c is the temperature of initiation of the reaction. When Equations 2 and 3 are substituted in Equation 1, the rate expression becomes:

$$d\alpha/dT = A(\lambda^2 N) kT/ha \exp(-\Delta H^\ddagger/RT) \exp(\Delta S^\ddagger/R). \quad [4]$$

When all of the temperature-independent constants except a are grouped and designated as k_o , the expression becomes:

$$d\alpha = (k_o/a)T \exp(-\Delta H^\ddagger/RT) dT.$$

From this expression, it is evident that the fractional area, α , developed under the thermal conductivity curve is:

$$\alpha = (k_0/a) \int T \exp(-\Delta H^\ddagger/RT) dT,$$

between the limits of the temperature of initiation of the reaction and that in question. When the upper limit is the time of completion of the reaction, α is equal to unity. The above integral is a non-standard one, but it may be evaluated by two $u.dv$ -type substitutions to yield:

$$\alpha = (k_1/a) T^3 \exp(-\Delta H^\ddagger/RT) [1 - 3 RT/\Delta H^\ddagger + 12 R^2 T^2/\Delta H^{\ddagger 2} \dots],$$

where the term in square brackets represents the first three members of a series. By taking logarithms and regrouping, the expression becomes:

$$\ln(\alpha a/T^3) = \Delta H^\ddagger/RT + \ln k_1 + \ln [1 - 3 RT/\Delta H^\ddagger + 12 R^2 T^2/\Delta H^{\ddagger 2} \dots].$$

Except for the term in square brackets, the equation is that of a straight line in $\ln(\alpha a/T^3)$ and $1/T$. From the slope of the relationship, the enthalpy of activation, ΔH^\ddagger , would be calculable if the term in square brackets were small and could be neglected. This term has been calculated for activation energies from 10 to 60 kcal.mole⁻¹ over the temperature range from 500 to 1000°K, as shown in Table II. The maximum error in ΔH^\ddagger caused by neglecting the term is 2% at 1000°K. with a ΔH^\ddagger of 10 kcal.mole⁻¹, and the minimum error is 0.1% at 1000°K. for an enthalpy of 60 kcal.mole⁻¹. Since even the 2% error is well within the range of other experimental errors, the term in square brackets may legitimately be neglected and activation energies calculated from either a $\log(\alpha a/T^3)$ versus $1/T$ plot or they may be resolved by a computer programme written to accept individual measurements of slices of the peak area, the initial experimental temperature and the rate of heating. Both methods have been used, with preference given to the computer programme because it permits the use of a large number of points (50 to 150) to establish the ΔH^\ddagger from a single run.

In Fig. 11, two Arrhenius lines are shown for the decomposition of CaCO_3 . The one referred to the right-hand axis was established with isothermal experiments, and that referred to the left-hand axis was established with programmed heating rates of 0.5, 1, 2, 3 and 4°C. min.⁻¹. The average of the results for the

five heating rates is shown, each being within the experimental error of ± 2 kcal. mole⁻¹. The agreement between the isothermal and programmed temperature methods is within the experimental error on each determination.

Conclusions

Gas analysis by thermal conductivity may be used to establish the thermodynamic and kinetic properties of certain types of heterogeneous decomposition reactions. Recent advances in equipment designed for gas analysis permit the rapid automatic acquisition of experimental data during non-working hours.

Acknowledgement

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TABLE I
Primary Apparatus Components

GOW-MAC Instrument Co. Thermal Conductivity Cell
Unit TR III A W2 with Power Supply Unit 405

Joseph Kaye and Co. Inc. Ice-Point Reference
System RJB-2C

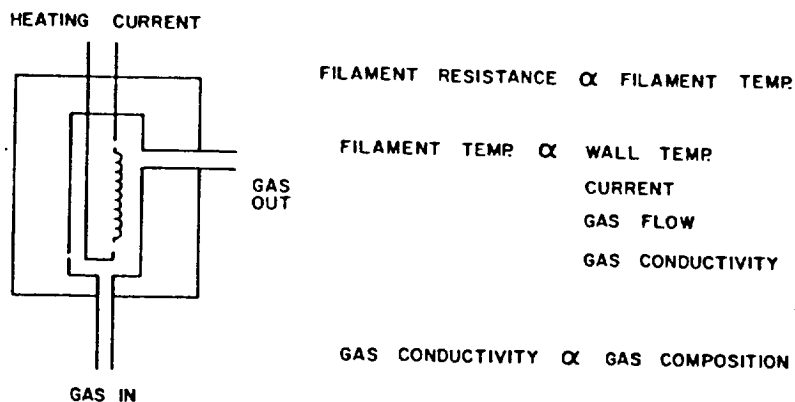
Hewlett-Packard Mosley Strip Chart Recorder
7100B

Infotronics Corp. digital integrator 471

F and M Power Proportioning Temperature
Programmer 240R

TABLE II
Approximate Errors of Estimate in ΔH^\ddagger

<u>ΔH^\ddagger</u> <u>(kcal/mole⁻¹)</u>	<u>T</u> <u>(°K.)</u>	<u>Approx. error</u> <u>(%)</u>
10	500	0.7
	1000	2.0
20	500	0.4
	1000	1.0
40	500	0.2
	1000	0.5
60	500	0.1
	1000	0.3



WHEN WALL TEMP, CURRENT, AND GAS FLOW ARE CONSTANT,

FILAMENT RESISTANCE \propto GAS COMPOSITION

Figure 1

Schematic diagram of thermal conductivity cell, showing filament mounted in stream of gas flowing through heated metal block.

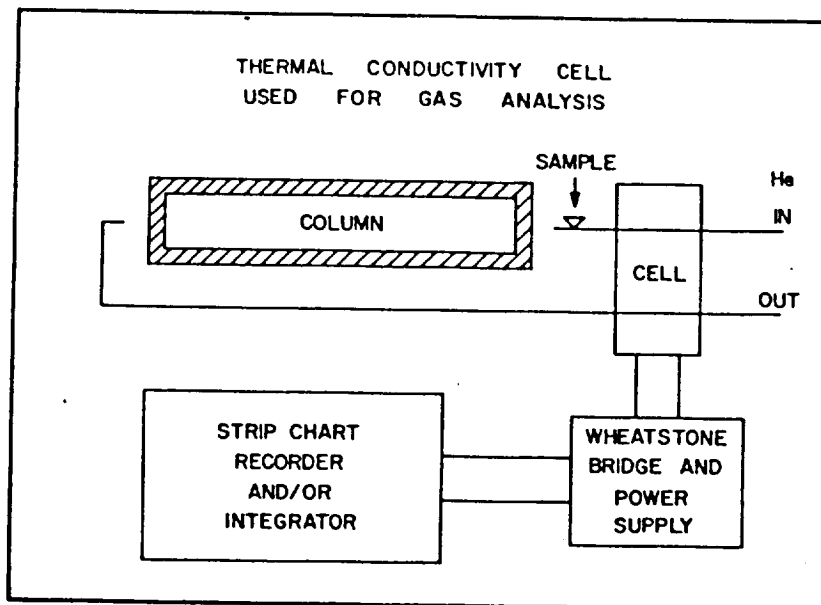


Figure 2

Schematic diagram of thermal conductivity cell incorporated in gas analysis apparatus.

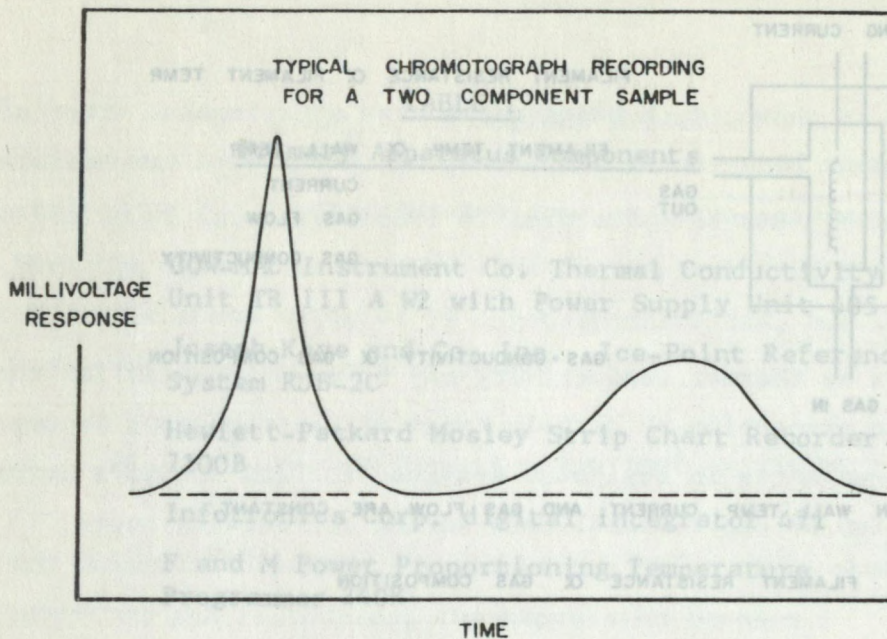


Figure 3

Typical response curves for plug samples of slightly-adsorbed (left) and strongly-adsorbed (right) gas components.

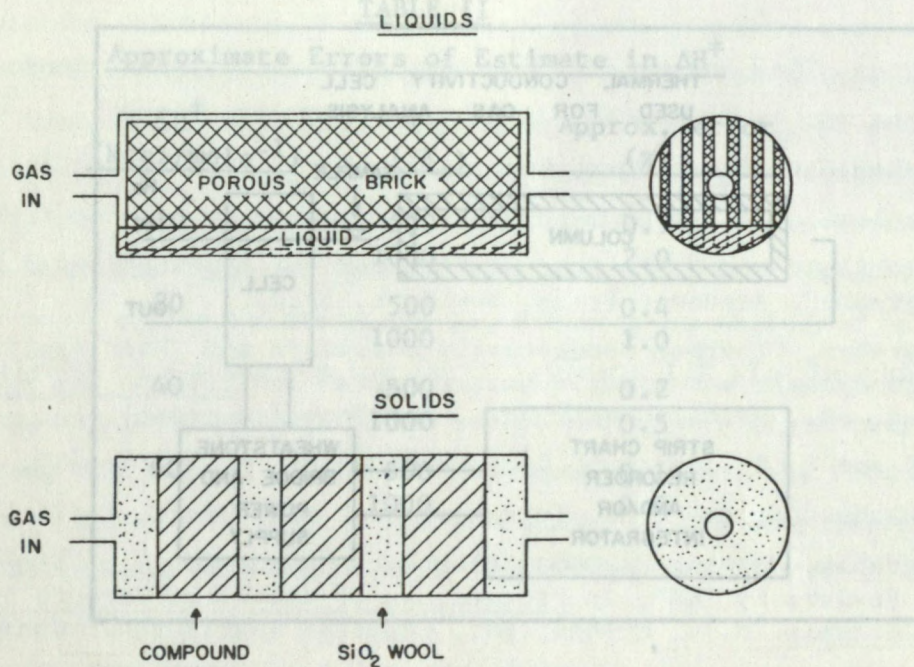


Figure 4

Sketch of columns used for saturating carrier gas with vapour or for establishing equilibrium decomposition pressures over solids.

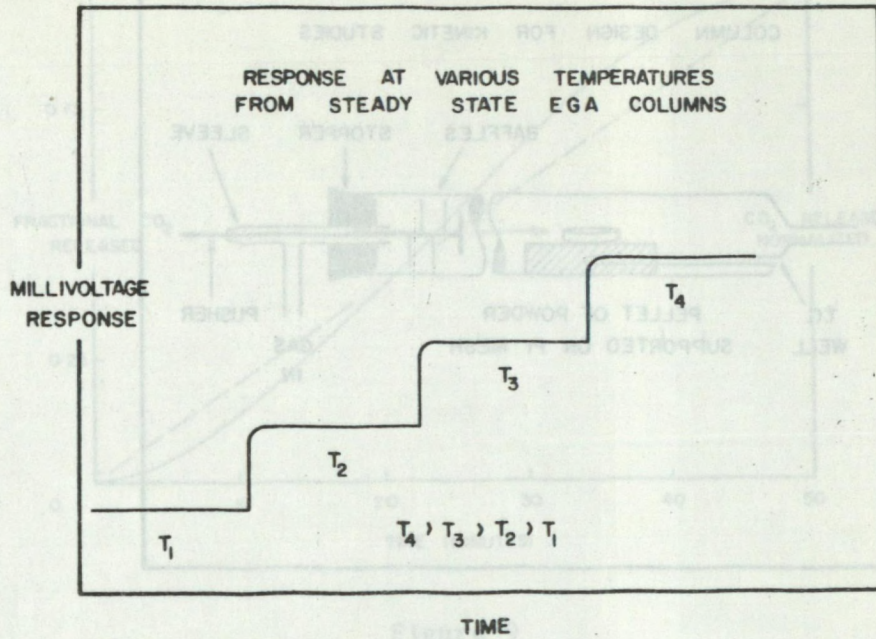


Figure 5

Steady-state response from a transpiration experiment at various temperatures.

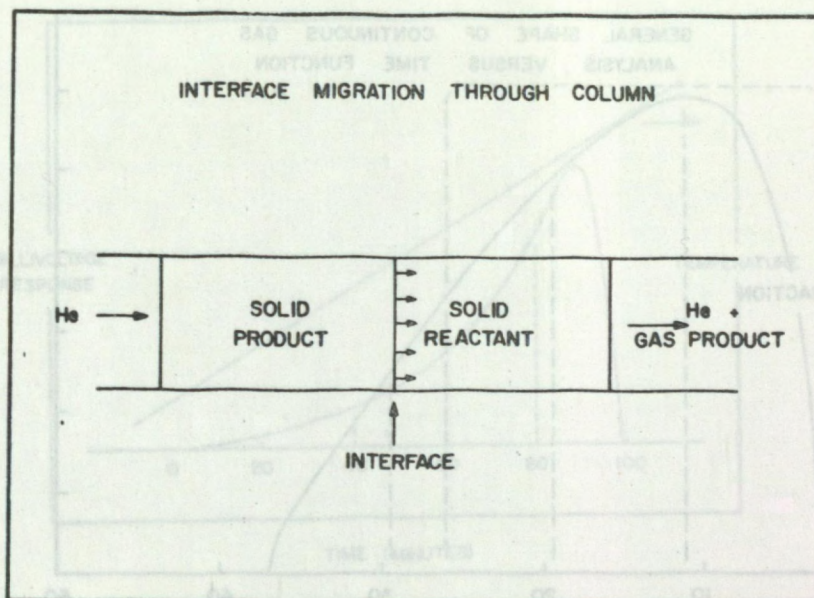


Figure 6

Sketch illustrating that the solid product of decomposition is not in contact with gaseous product of decomposition.

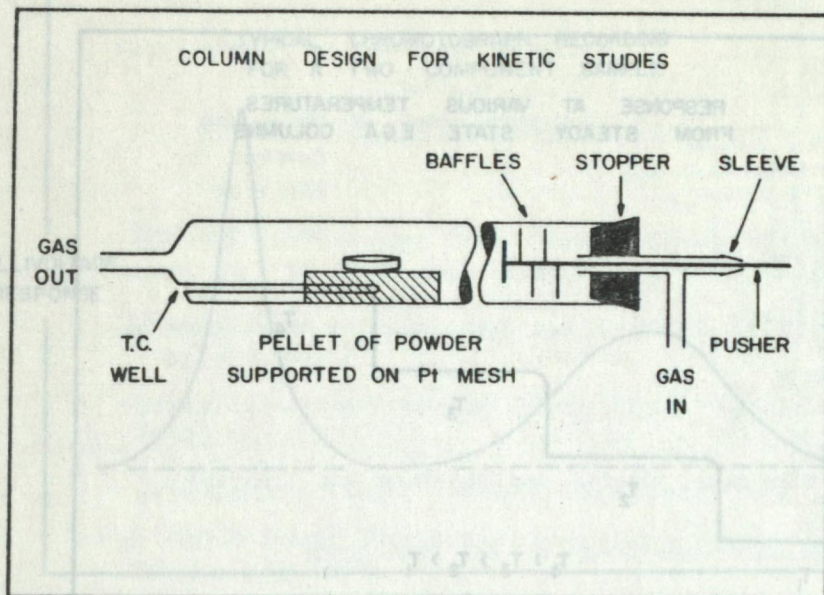


Figure 7

Schematic diagram of cell for both isothermal and linearly programmed temperature experiments.

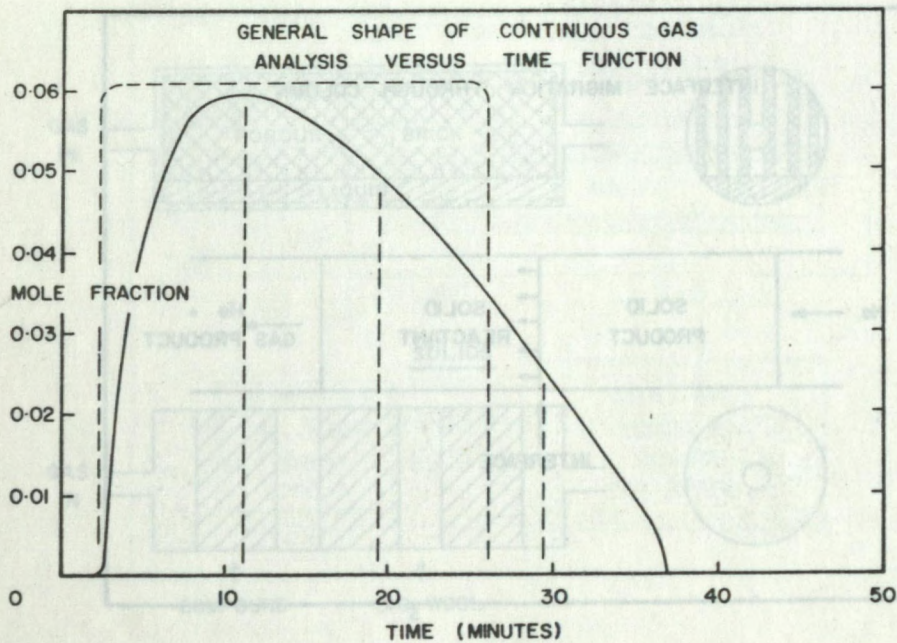


Figure 8

Typical mole fraction-time response curve. Rectangular dotted line would be approached if there were no change in sample geometry.

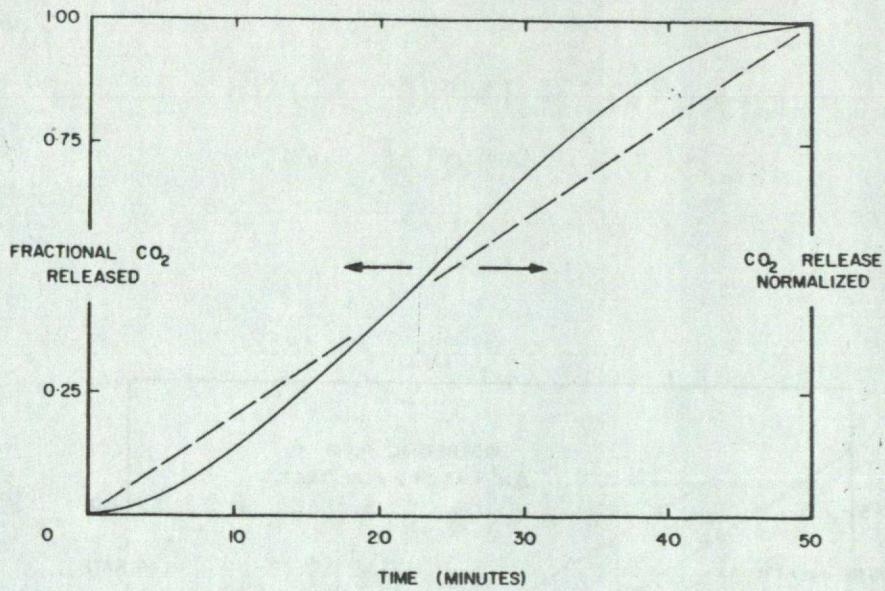


Figure 9

Typical curve for an isothermal kinetics experiment: original response (solid line) and normalized response (dotted line).

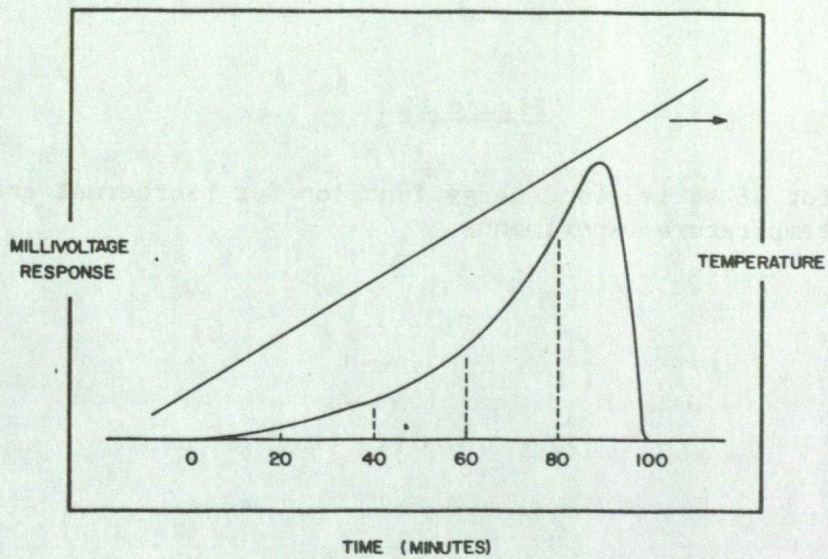


Figure 10

Typical response curve for a linearly programmed increasing temperature kinetics experiment.

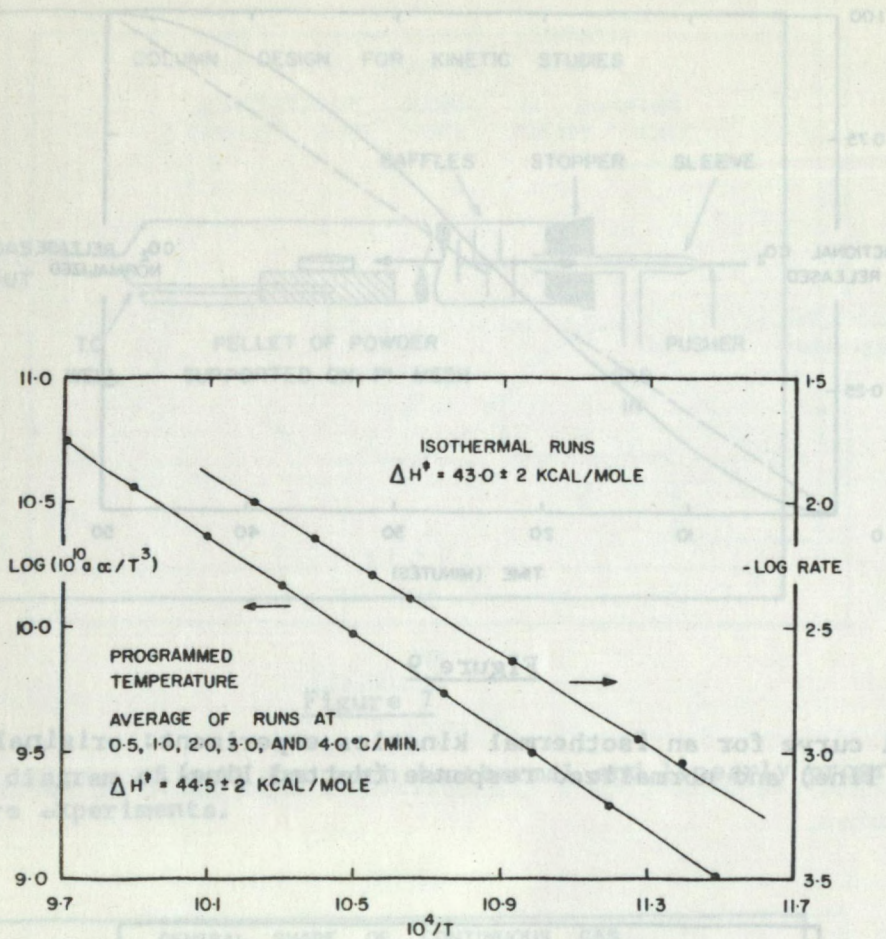


Figure 11

Arrhenius plot of activation energy function for isothermal and linearly-programmed temperature experiments.