rate of carrier gas; and (c) having increased detector sensitivity. In all such cases the sample size would have to be large enough to scrub the carrier gas stream sufficiently well to approach equilibrium both of the sample with the gas stream and of the gas stream with the sample, i.e., to minimize bypassing of the sample by a significant portion of the exit gas.

The present method is well adapted for activated carbons, for which the Polanyi-based estimation method is quite accurate for transposing adsorption data over a wide temperature range. It is also readily adapted to the more conventional use of nitrogen as the adsorbate at cryogenic temperatures, with helium or hydrogen as the carrier gas. Moreover, although it is here illustrated for activated carbon, it should be readily applicable to any solid of relatively high surface area and heterogeneous surface for which we can use the Polanyi theory (or any other workable method) to calculate an isotherm from nonisothermal data.

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Personal Vinyl Chloride Monitoring Device with Permeation Technique for Sampling

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A method for measuring the exposure of personnel to vinyl chloride has been developed which utilizes the permeation technique for sampling. The vinyl chloride that permeates the membrane is trapped on activated charcoal which is removed for subsequent determination by gas chromatography. The monitor is about the size of a standard film badge, weighs less than 35 g, and requires no source of power. The method is insensitive to temperature and humidity, and is free of significant interferences. The method is ideally suited to personal monitoring programs required by OSHA regulations, because the analytical data represent a time-weighted-average exposure and require no further data reduction step.

The health hazards posed by vinyl chloride (chloroethene) vapor in the industrial environment have received broad coverage in both the scientific and public press. The fact that the deaths of some 28 workers have been attributed to chronic exposure to high concentrations of vinyl chloride has resulted in stiff Federal regulations covering this hazard. Current standards (*1*) call for an action level of 0.5 parts-per-million time-weighted-average (TWA) exposure, which, if exceeded, requires the implementation of an extensive personal monitoring program. This directive permits a maximum allowable 8-h TWA exposure of 1 ppm and a maximum permissible exposure of 5 ppm for no more than 15 min. These regulations create the need for a simple, inexpensive method for measuring time-weighted-average exposures of personnel to vinyl chloride. A method has been developed to meet these needs. The approach employs a sampling device based on the permeation principle, and an analytical finish utilizing gas chromatography.

Previously published methods for making vinyl chloride determinations have been of two basic types, area monitors and personal monitors. Area monitors have been widely used for determination of contaminants in the ambient air of the working environment. Typically, they utilize a gas chromatograph with a continuous automatic sampling system. The system is capable of making a fixed number of determinations per hour and requires data analyses to provide a time-weighted-average for concentration. Other area monitors rely on a long-path infrared analyzer for the determination and give a continuous record of the contaminant level. Again, data reduction is necessary to produce a time-weighted-average. Either system represents an initial investment of thousands of dollars for equipment and requires periodic maintenance for sustained operation. While they provide instantaneous readings of the vinyl chloride level in the ambient air, they cannot effectively monitor the air inhaled by the individual worker, which is subject to such localized effects as leaking and venting of equipment.

Methods for personal monitoring developed to date have all relied on the collection of vinyl chloride by either drawing air over a suitable adsorber such as activated charcoal (*2*, *3*), or drawing air into a gas sampling container at a known constant rate. Most of these methods require the use of a battery-powered pumping system which is often heavy, noisy, and quite cumbersome. Methods employing collection of the air sample within a container also require that the worker wear this bulky container in addition to the aforementioned pump. These various personal monitoring systems are all inconvenient and uncomfortable and, in many cases, may also prove to be hazardous in their own right because of their unnecessary bulkiness.

A new sampling method is now proposed which employs a small, light-weight, reusable, and uncomplicated personal monitor that does not require a source of power. The sampling device is a badge having dimensions of 41 mm by 48 mm and a thickness of 7 mm (Figure 1). An internal cavity is covered by a permeable membrane through which vinyl chloride passes at a rate proportional to the external concentration. The vinyl chloride that permeates through the membrane is adsorbed on activated charcoal which is later removed from the device after completion of the exposure, and the amount adsorbed is then determined by gas chromatography. There are no

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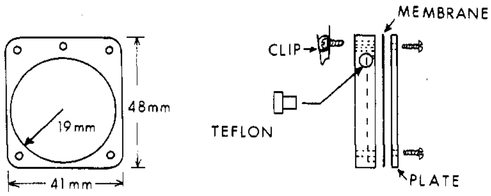

Figure 1. Personal monitoring device

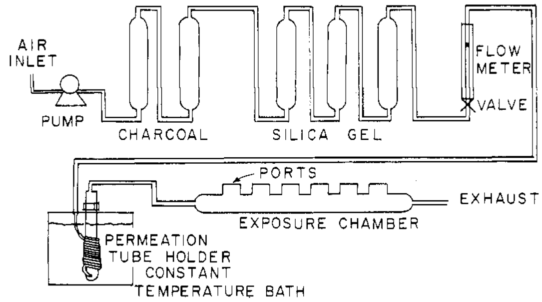

Figure 2. Calibration apparatus

known interferences, variations in temperature and humidity have had no effect and there is linear response over the range of 5 ppb to 50 ppm. Sampling times of 10 min to 24 h or longer are possible. Naturally, with the shorter sampling times higher detection limits will be observed.

EXPERIMENTAL

Preparation and Calibration of the Permeation Device. The permeation device used for the initial feasibility studies in this work was the same as that described previously (*4*), except the absorbing solution was replaced by a known quantity of activated charcoal which served as an adsorber for the vinyl chloride that permeated the membrane.

The membrane material used for the device was a disk of single-backed dimethylsilicone rubber (General Electric Co., One River Road, Schnectady, N.Y. 12305). The material was not entirely of uniform thickness; hence, each permeation device under study was individually calibrated using the apparatus illustrated in Figure 2. Calibration was accomplished by cleaning and dehumidifying air from the laboratory by pumping it through columns of activated charcoal and silica gel. Finally, the clean, dry air was passed at a predetermined flow rate over a permeation tube, of the design of O'Keeffe and Ortman (*5*). The permeation tube emitted vinyl chloride at a known constant rate, thereby providing a primary standard for the calibration procedure. The standard concentration of vinyl chloride in air was passed through the exposure chamber where the permeation devices were exposed for calibration.

Design and Preparation of Standard Permeation Tubes. Wherever possible, the standard permeation tube described by O'Keeffe and Ortman (*5*), and Scaringelli et al. (*6*) was used for the study of both vinyl chloride and possible interferences. These tubes proved unsuitable for studies at very low levels; therefore, for concentrations below 0.05 ppm, it was necessary to use a low-level permeation tube which was similar to the reservoir device of Saltzman et al. (*7*).

A reservoir of 3 mL was used with an active tube length of as little as 1 mm. This device, which has been used successfully for other gases, has a very short active area and was capable of accurately dispensing levels as low as 20 ng/min of vinyl chloride. Permeation tubes containing vinyl chloride had a tendency to form a solid material, presumably a polymeric species, despite precautions taken to entrap inhibitor within the tube. This was not found to present a serious problem as long as there was liquid visible in the tube.

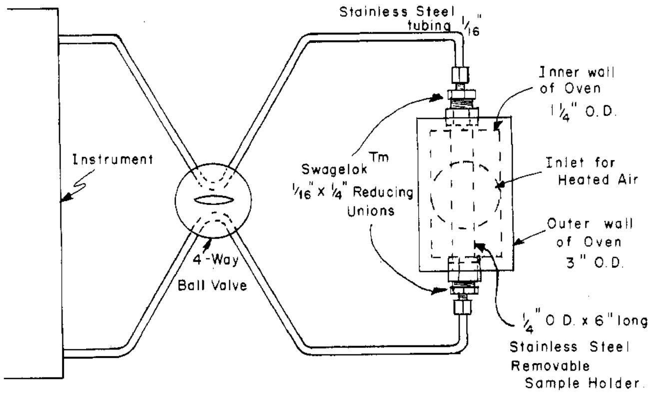

Figure 3. Apparatus for thermal desorption of vinyl chloride

The study of some possible interfering species, particularly those with low vapor pressures, showed that the standard permeation method of dispensing the substance of interest was not always feasible. In order to study these substances, diffusion tubes were used (*8*). A glass tube was prepared having one end sealed and the other drawn to a small capillary. The tube was then filled with the liquid of interest and allowed to come to equilibrium, at which time the substance diffused through the capillary at a constant rate determined by the temperature and the length of the capillary. The diffusion tubes were calibrated gravimetrically in the same manner as the permeation tubes. They were used for dispensing substances that had vapor pressures of less than 1 atm at the temperature at which they were maintained. The diffusion rates were found to be stable over periods of up to six months, as long as there was liquid in the tube.

Reagents. All gases used in the preparation of permeation tubes were chemically pure grade. All liquids used were reagent grade. Purity of each organic reagent was checked by gas chromatography.

Adsorber. The adsorber used for these experiments was Darco Activated Charcoal, 20–40 mesh, supplied by Matheson, Coleman and Bell. It was pretreated to remove moisture and any organics present by heating to 350 °C under a flow of inert gas. No vinyl chloride was found or any charcoal following this treatment.

Instrumentation. A Varian Model 1200 gas chromatograph along with a Honeywell-Brown recorder equipped with a Disc integrator was used in all investigations. The gas chromatograph was equipped with a flame ionization detector and was modified to permit the use of an external sampling system (Figure 3) consisting of an interchangeable sampling loop in a thermally shielded compartment which could be rapidly heated to 300 °C. The sample loop consisted of a 15 cm × 6.35 mm o.d. stainless steel tube. The tube was placed inside a brass tee and was heated by the exhaust from a heat gun, (Master Appliance Corp., Model No. HG-501) being directed through the side of the tee. A four-way valve provided a bypass for the helium carrier gas to permit changing of the sample loop without interrupting the determination.

Standards for Instrumental Calibration. The response factor of the gas chromatograph was determined by preparing a standard containing a known amount of vinyl chloride adsorbed on 1 g of activated charcoal. This was accomplished by collecting the vinyl chloride from a stream of known concentration by passing the standard through a tube containing the charcoal sample. A backup tube was used to assure that no breakthrough of vinyl chloride occurred. These were then analyzed along with the unknown samples. This provided an accurate measure of the response of the instrument to the levels of vinyl chloride being determined. It also compensated for the fact that vinyl chloride may not be completely desorbed from the charcoal. No breakthrough of vinyl chloride was observed for any standard studied over the range of 0.2 to 200 ng.

Calibration of the Permeation Devices. As stated previously, it was necessary to calibrate each permeation device individually. This was accomplished by exposing the device to a known concentration of vinyl chloride in air. Subsequent determination of the amount of vinyl chloride adsorbed on the charcoal from the device allowed the calculation of a permeation constant for each device. This constant was calculated from the following equation:

$$k = \frac{Ct}{w} \qquad (1)$$

where k = constant (about 0.5); C = concentration of vinyl

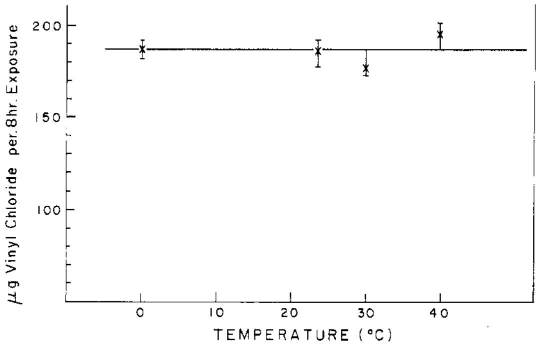

Figure 4. Effect of temperature on permeation of vinyl chloride

chloride, ppm; t = time of exposure, and w = amount of vinyl chloride adsorbed, μg. This constant, which with care can be determined to a precision of 3%, was used for the calculation of the average concentration of vinyl chloride in an unknown atmosphere by using the equation:

$$C = \frac{wk}{t} \tag{2}$$

where C = time-weighted-average vinyl chloride concentration, ppm.

Method for Chromatographic Analysis. The chromatographic determination of vinyl chloride used for these studies primarily employed the thermal desorption process. The charcoal sample was placed in a sample loop and the loop mounted in the desorption oven. Standards were first transferred to a vial, then to the sample loop. The column was cooled to 25 °C and the sample loop purged with the helium carrier gas. Then, with the carrier gas still flowing through the sample loop, the loop was heated by the hot air from the heat gun. The conditions necessary for optimum desorption were found to be 5 min desorption at 300 °C.

After the completion of the thermal desorption process, the vinyl chloride from the sample was trapped on the head of the analytical column. For the experiments described herein, this column was a 2-m by 2.4 mm i.d. stainless steel tube packed with Chromosorb 102 (Johns-Manville). The carrier gas flow was shunted around the sample loop by the bypass valve, and the column oven heated to 90 °C. Under these conditions, vinyl chloride exhibited a retention time of ~4 min. After the emergence of the vinyl chloride, the column was heated to 200 °C to remove other substances and ready the column for the next determination. Carbon disulfide extraction and analysis procedures as recommended by NIOSH (*3*) were also found to be applicable for use with the permeation sampling technique. One successful procedure involved extraction of the charcoal with 5 mL of CS_2 in a vial sealed with a Teflon-backed rubber septum. The mixture was allowed to develop for 30 min with periodic agitation. Both the sample and solvent were chilled to dry ice temperatures before extraction, and sample vials were sealed with Teflon-backed rubber septum.

RESULTS

Temperature Effect. Previous studies of the permeation phenomenon have disclosed a variety of temperature effects for different compounds. For sulfur dioxide there was a very small negative effect (*4*) and for carbon monoxide a rather large positive effect (*9*) was observed. To determine the effect of temperature on the permeation rate of vinyl chloride, exposures were made to a fixed concentration of the gas at temperatures of 0, 23, 30, and 40 °C. This covered the range of temperatures most likely to be found in facilities producing vinyl chloride or its related products. The results of this study are presented in Figure 4. All values found fell within the range of experimental error for the determination, thus indicating no measurable temperature effect.

Response of the System to Various Vinyl Chloride Levels. A major concern when this study was begun was the ability of the activated charcoal to completely adsorb the vinyl chloride permeating through the membrane. All previous permeation studies had involved the chemical reaction of the species permeating through the membrane with an absorbing solution, removing it irreversibly from the system. For the study of vinyl chloride, a suitable liquid reagent could not readily be found; therefore, the use of activated charcoal was investigated and proved satisfactory.

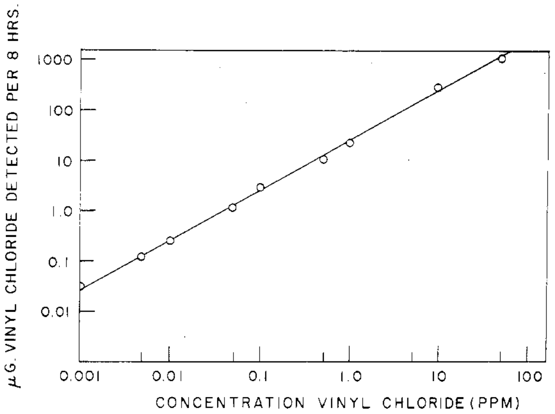

Figure 5. Response of the permeation device to various levels of vinyl chloride

The concentration range studied in this work was to a large degree determined by the experimental limits of the method used for preparation of the standard vinyl chloride concentrations. Fortunately, the upper limit of 50 ppm corresponded with the previous Federal standard, and was more than an order of magnitude higher than the maximum level permitted under the current standards. The lower limit was set at 1 ppb because it was not possible to accurately produce levels of vinyl chloride below this concentration using our methods. The response of the system to vinyl chloride, as illustrated in Figure 5, was linear over the entire range studied. Also, even at the limit of 1 ppb, precision was within the ±50% limit specified by NIOSH for an acceptable method of analysis. The precision above 0.1 ppm for an 8-h sample was 5% for thermal desorption while the carbon disulfide procedure yielded a precision of about 5% at 0.5 ppm.

Response Time. Permeation depends on three independent processes, dissolution of the gas by the membrane, diffusion through the membrane, and evaporation of the gas from the membrane. The success of the endeavor depended on the rate at which the system attained an equilibrium state between these three processes. Therefore, studies were made to determine how rapidly the membrane responded to changes of vinyl chloride exposure. For this determination, a permeation device was exposed to a constant level of vinyl chloride in the system. Every 10 min, the charcoal adsorber inside was removed and replaced with fresh adsorber. The length of time required to attain a constant rate of permeation through the membrane is indicated by the amount of vinyl chloride found on each fraction. No detectable differences were observed for any of the samples collected (Figure 6). This indicated that the start of permeation of vinyl chloride through the silicone rubber membrane was very rapid because permeation is initiated by a sudden breakthrough rather than a gradual increase. The estimated upper limit of the response time, based on the precision of the determination (5%), was 30 s or less.

Humidity Effect. As in all previous studies, the preliminary work was done in a system having a near zero relative humidity. For real analyses, particularly in the Gulf Coast area where the majority of the vinyl chloride monomer used in this country is produced, this was an artificial situation. Humidity was not expected to interfere with the analysis but, to confirm this presumption, studies were made at a relative

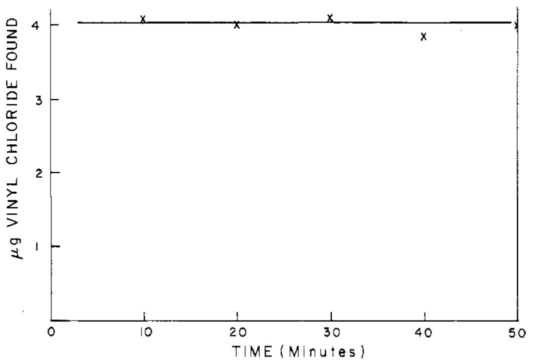

Figure 6. Response time of the permeation device to vinyl chloride

Table I. Effect of Common Interferents on Vinyl Chloride Determination

Interferent	Interferent concn, ppm	Vinyl chloride found, µg	Deviation, %
None	...	10.40	...
Sulfur dioxide	4.5	10.40	0
Nitrogen dioxide	3	10.54	+1.30
Ozone	2	10.82	+4.0
Chlorine	37	10.68	+2.7
Ethylene dichloride[a]	3	20.80	+100
Ethylene dichloride[b]	3	10.96	+5.4

[a] Vinyl chloride determined by thermal desorption.
[b] Vinyl chloride determined by carbon disulfide extraction.

humidity of 100%. No detectable differences were observed between the response from these studies and those at zero relative humidity for the same level of exposure.

Interference Studies. Interference studies were run on several common pollutants that may be encountered in the vicinity of plants producing vinyl chloride. These included sulfur dioxide, nitrogen dioxide, ozone, ethylene dichloride, and chlorine. The results of these studies are summarized in Table I. In every case except for that of ethylene dichloride, the deviation observed between the experiment using only vinyl chloride and that incorporating a possible interferent was within the experimental error of the technique. However, for the case of the ethylene dichloride, a large positive interference was observed when the thermal desorption method was used for the vinyl chloride determination. It was immediately confirmed by a subsequent experiment, that pure ethylene dichloride produced a large chromatographic peak corresponding to vinyl chloride when it was thermally desorbed from charcoal. Further experimentation, utilizing the carbon disulfide extraction procedure, resulted in the elimination of the interference by ethylene dichloride.

Storage of Samples. The monitor may be stored in an air-tight container for at least 8 h without loss of vinyl chloride. However, for longer storage, the charcoal should be transferred to a sealed vial. Samples stored in vials for periods up to 6 months have shown no significant losses. It would not be advisable to store samples collected in a complex environment for this length of time. It should also be noted that with monitors that were exposed to uncontaminated air for 8 h, no detectable losses were observed indicating that desorption through the membrane must be very slow.

DISCUSSION

Although the thermal desorption approach was used for the most part in these studies, it has two major drawbacks. First, it does not allow room for a mistake, since all of the sample is utilized in the analysis. For this reason the alternate procedure of using carbon disulfide extraction has some merit as long as the higher detection limit of 20 parts-per-billion time-weighted-average exposure for at least an 8-h period can be tolerated. Secondly, and most importantly, thermal desorption from untreated activated charcoal is not feasible wherever there exists the possibility of any exposure to ethylene dichloride. This compound undergoes an elimination reaction on heating of the charcoal, producing hydrogen chloride and vinyl chloride, thus producing an undesired positive interference.

Table II. Effect of Geometry on Thermal Desorption of Vinyl Chloride

Location within tube	Integrator counts obsd
Top	30
Uniform	400
Bottom	1070

Another interesting discovery was made during the course of this study. It was observed that the geometry of the sample containing the standard had a pronounced effect on the amount of vinyl chloride desorbed by the thermal method. When the sample holder was used for the collection of the standard and then transferred directly to the thermal desorption unit, most of the vinyl chloride was on the charcoal in the extreme upper part of the tube, near the carrier gas inlet. Subsequent analysis gave surprisingly low results. When the transfer of the charcoal was accomplished by interconnection of the collection tube and the sample holder by a short piece of Teflon tubing, most of the vinyl chloride was adsorbed on charcoal near the bottom of the holder. Very high results were obtained in these cases. Finally, transfer of the charcoal to a vial where it was mixed gave a uniform distribution of vinyl chloride throughout the sample holder, much like that found with charcoal from the permeation device. This procedure allowed reproducible results to be obtained with apparent vinyl chloride recoveries between those obtained with the other two procedures. These results are presented in Table II. Heating the samples for a longer period of time, up to 20 min, did not increase the response. Treatment of the charcoal with hydrogen and heat to reduce any possible reaction sites also had no effect on the desorption efficiency. Gas chromatography–mass spectrometry proved that one reason for this effect was the formation of polymeric species. The vinyl chloride dimer and trimer were clearly observed, and evidence of the tetramer was found. Therefore, when using thermal desorption to determine vinyl chloride, it is essential to calibrate the instrument by a procedure as much like that used for analysis as possible.

It may also be noted that the device described here affects only the method of sampling for vinyl chloride. Almost all laboratories that are currently using charcoal adsorption tubes for determination of vinyl chloride in their personal monitoring programs can use this method with no significant changes in their present procedures for the analytical finish. All criteria for an analytical method for vinyl chloride determination in personal monitoring programs set forth by NIOSH have been met. Convenience to the wearer is a significant feature of the device. Field studies have indicated an enthusiastic acceptance of the method by those workers who have previously used other methods. The initial findings of field evaluations have confirmed the validity of the method.

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Differential Thermal Analysis and Reaction Kinetics for *n*th-Order Reaction

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Relationships are derived for determining the three kinetic parameters from a single DTA curve for a general *n*th-order reaction, and for predicting the DTA curves from the known kinetic parameters. Gorbachev's approximation for the integral of the Arrhenius exponential function is used. The relationships have been applied to a solid–gas reaction and decomposition reactions in solid-state and in aqueous solution. Fair agreement between the rather simple theories and the experimental data was obtained.

The subject of determining kinetic parameters from differential thermal analysis (DTA) data has attracted considerable attention and interest. Comprehensive reviews on this subject and discussions on related problems have been made by Barrall (*1*), Blazek (*2*), Wendlandt (*3*), etc.

In a previous study (*4*), quantitative relationships between the kinetic parameters and the characteristic temperatures of a DTA curve were derived for the first-order reactions. However, it is obviously more desirable to evaluate the kinetic parameters for a general *n*th-order reaction without a priori knowledge of the value of the order. In this work, relationships are derived for evaluating the three kinetic parameters, i.e., reaction order, activation energy, and frequency factor from a single DTA curve and, conversely, with known kinetic parameters, the DTA curve will be predicted. The approximation proposed recently by Gorbachev (*5*) for the integral of the Arrhenius exponential function has been used in the derivations and it was shown to be superior to that by Frank-Kamenetskii (*6*). This approximation has also been shown by Gorbachev (*5*) to be more accurate than that by Coats and Redfern (*7*).

The application of the method outlined in this work is demonstrated for a gas–carbon reaction and the decomposition reactions in the solid state and in aqueous solution. All the reactions are assumed to follow the simple rate expression shown in Equation 1. It is also noted that deduction of the mechanism of the reaction is not attempted in this study.

THEORETICAL CONSIDERATIONS

The rate expression for a general *n*th-order reaction is:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = r_0(1-x)^n e^{-E/RT} \tag{1}$$

where x is the fractional completion of the reaction; t, the time; r_o, the frequency factor; n, the order; E, the activation energy; R, the gas constant; and T, the absolute temperature.

It is assumed that the temperature differential (ΔT) in a DTA curve can be approximated as being proportional to the mass reaction rate and is expressed as the following:

$$\Delta T = k_1 r_0 m_0 (1-\mathrm{x})^n e^{-E/RT} \tag{2}$$

here m_0 is the initial mass of the reactant and k_1 is the proportionality constant which can be approximated as the heat of reaction divided by the total heat capacity of the sample mass.

The validity of Equation 2 has caused considerable controversy in the past. On the one hand, Equation 2 has been assumed in DTA involving some gas–solid and solid decomposition reactions, as in the classic work by Murray and White (*8*), by Kissinger (*9*), and by others. On the other hand, in DTA involving phase transitions, the reactions were terminated at the peak temperatures and Equation 2 is not applicable (*10–12*). However, by using simultaneous DTA–DTG techniques, for the types of reactions that will be discussed in this work, it has been clearly shown that the DTA and the DTG correspond quite well (*13*). Detailed analyses of the various reaction systems in connection with the validity of Equation 2 will be published elsewhere. It is noted here Equation 2 is indeed a good approximation to the reaction systems herein studied.

For a DTA curve with a linear heating rate k_2, $\mathrm{d}t = \mathrm{d}T/k_2$. Equation 1 can be rewritten with the above substitution and integrated as the following:

$$\int_0^x \frac{\mathrm{d}x'}{(1-x')^n} = \frac{r_0}{k_2}\int_0^T e^{-E/RT'}\,\mathrm{d}T' \tag{3}$$

In integrating the Arrhenius exponential function, the approximation by Frank-Kamenetskii has been adopted previously (*4*). It has been found since then that the approximation for the integral proposed recently by Gorbachev (*5*) is more suitable for the kinetic analyses of the DTA data because of its simpler form and perhaps higher accuracy under normal conditions. By using Gorbachev's approximation:

$$\int_0^T e^{-E/RT'}\,\mathrm{d}T' = \frac{RT^2}{E+2RT}e^{-E/RT} \tag{4}$$

the following solution is obtained for Equation 3: