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THERMAL HAZARD EVALUATION OF STYRENE POLYMERIZATION BY ACCELERATING RATE CALORIMETRY

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The thermal polymerization of inhibited styrene monomer is investigated by Accelerating Rate Calorimetry (ARC). The time-temperature-pressure data generated by this technique are utilized in evaluating the thermal hazards associated with the industrial processing of styrene monomer. Several examples are given on the interpretation and application of ARC data to environments ranging from lab to plant-scale conditions including discussions concerning the similarities and dissimilarities between the ARC and large-scale equipment. The polymerization of styrene monomer is also used to evaluate the performance of the ARC over a broad temperature range, 80 – 300 °C. The data indicate that removal of the radiant heater assembly yields better agreement between the heat of polymerization of styrene as measured by the ARC and corresponding values from the literature. This effect is believed to be observable only under conditions of low reaction rates for long periods of time such as in the case of styrene monomer.

The evaluation of thermal and pressure hazards associated with the manufacture, transport, and storage of chemicals is an important area of research in the chemical industry. The engineering design of equipment to prevent, control or withstand runaway reactions which result in pressure increase is of great concern from a safety and loss point of view. In order to design a piece of equipment which will operate safely during an emergency situation, it is necessary to have data on the kinetics, thermodynamics, and physical properties of the potential runaway reaction.

Several approaches have been utilized in the past to obtain information on the kinetics of exothermic reactions. One of the most commonly used techniques in thermal hazard evaluation is differential scanning calorimetry (DSC) which can yield both the heat of reaction and the kinetics of the reaction of interest [1]. A modification of the sample container used in DSC has been developed to handle volatile chemicals or materials which generate gaseous products on decomposition, conditions which are common in the chemical industry [2]. However, one limitation to the DSC methods for hazard evaluation is the difference in experimental conditions compared to normal operating conditions in a chemical plant. DSC data are obtained at a fixed heating rate which forces the reaction to occur at higher temperatures in the DSC than would be experienced during processing or storage. As a result, the experimental data often must be extrapolated to normal operating temperatures. Isothermal DSC experiments must be used to validate this extrapolation to lower temperatures. In addition, pressure data are not commonly available by DSC techniques.

Other instruments have also been developed for thermal hazard evaluation, such as Sedex [3], bench scale calorimeter [4], adiabatic runaway device [5], and the large-scale test device [6]. None of the above instruments, however, is either commercially available or in wide-spread use to date.

The first commercially available instrument to be widely used in the evaluation of thermal runaway reactions is the Accelerating Rate Calorimeter (ARC). This instrument is designed to obtain time-temperature-pressure data on a small-scale runaway reaction. In this paper, ARC data on styrene monomer will be presented and applied to specific problems which might be of concern in the chemical industry.

Experimental

The Accelerating Rate Calorimeter (ARC) was developed by the Dow Chemical Company and was licensed to Columbia Scientific Industries of Austin, Texas which currently markets the instrument under the trademark CSI-ARC^{TM}. Since details of the design, operation, and performance of the ARC have been published elsewhere [7–9], only a brief description of the device will be given here.

The operation of the ARC involves a container which with its contents is maintained adiabatic with respect to its environment. This is accomplished by monitoring the temperature of the sample container and adjusting the temperature of the surroundings so that there are minimal heat gains or losses from the container. In order to achieve an adiabatic environment over a temperature range of ambient to 400 or 500° and temperature rates of between 0.02° to 10°/min, the ARC utilizes a rather complex digitally controlled thermocouple/heater feedback system [8]. Figure 1 illustrates the calorimeter part of the ARC. The cylindrical temperature chamber consists of three controlled zones, top, side, and bottom, which contain the control heaters and thermocouples. The sample container or "bomb" is attached to a pressure feed-through fitting on the top of the chamber so that the pressure of the sample may be monitored throughout the experiment. The inside thermocouple is optional but is useful under conditions where the outside thermocouple or bomb thermocouple cannot give accurate temperature readings of the contents of the container [9]. The radiant heater, located in the bottom of the adiabatic chamber is used to heat the sample container to the starting temperature for the experiment.

Figure 2 gives a typical temperature-time profile for an ARC experiment. The first step is to enter "heat" mode and to heat the sample and container to the starting temperature of the experiment using the radiant heater. In this case the calorimeter is heated from ambient to 50°. After reaching 50° the calorimeter enters "wait" mode where the radiant heater is disabled and the calorimeter is allowed to thermally stabilize for a minimum of ten minutes. Next comes "search"

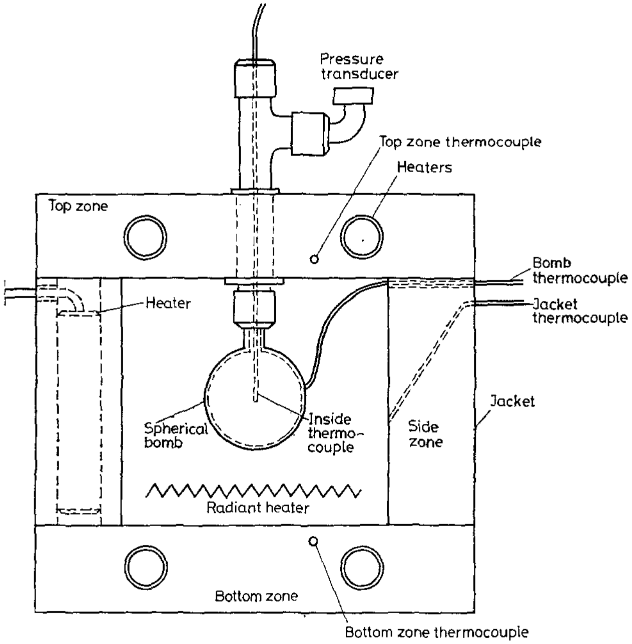

Fig. 1. Design of ARC calorimeter body

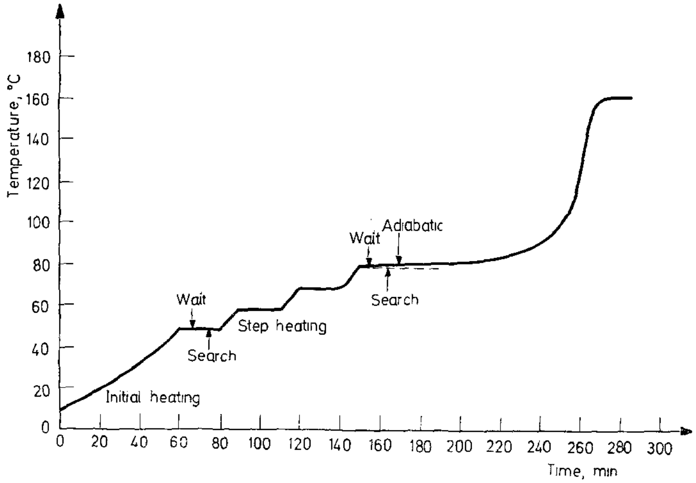

Fig. 2. Typical temperature *vs.* time plot of ARC experiment. The heat-wait-search operation mode of ARC

mode where the rate of temperature increase of the sample container is monitored. If this self-heat rate is below the operator set detection threshold, typically 0.02 degree/min, the calorimeter enters "heat" mode once more and increases the sample temperature by a given increment, in this case, 10°. This process of "heat-wait-search" is continued until a self-heat rate above the threshold is observed. For the case shown in Figure 2, the exothermic reaction is first detected at 80°. When an exothermic reaction is detected the calorimeter maintains the sample container adiabatic and does not add any more heat to the sample. Any increase in temperature is attributed to the self-heating of the sample. As the sample reacts, heat is produced and the temperature of the sample and bomb increase. When the sample temperature increases the reaction rate increases, typically in an exponential-like fashion until the reacting materials are consumed and the self-heating rate of the sample drops below the detection threshold. The calorimeter again enters its "heat-wait-search" mode of operation and continues to look for more exothermic activity of the sample. When the temperature exceeds the preset "end" temperature for the experiment, the run is terminated and cooling air is automatically applied to the sample container and surroundings.

All ARC experiments presented in this paper utilized Aldrich styrene monomer, 98–99% pure, containing 10 to 15 ppm *t*-butyl catechol (TBC) as a polymerization inhibitor. Whether titanium, Hastelloy C or nickel, all sample containers were one inch nominal internal diameter spheres with a one inch long by 1/8 inch outside diameter tube attached to the bomb for pressure measurement purposes. Details of the experimental procedure can be found elsewhere [10].

Molecular weight analyses were carried out by dissolving 0.25% by weight polymer in tetrahydrofuran (THF) and analyzing the resultant solution on a Waters Model 202 Gel Permeation Chromatograph (GPC) equipped with Dupont size exclusion columns, PSM 60-S and 1000-S, UV detector at 254 nm and THF solvent flow rate of 1.0 ml/min. The polymer standard used was a Dow 1683 polystyrene.

The measurement of styrene monomer, dimer, and trimer residuals was carried out on a Hewlett–Packard Model 5830A Gas Chromatograph equipped with a Model 18850A Hewlett–Packard Integrator.

Differential scanning calorimetric (DSC) analyses were run on a Dupont 910 DSC controlled by a Dupont 990 temperature programmer. The DSC technique employed in measuring the heat of polymerization of styrene has been described previously [2] and utilizes a 4.0 mm spherical glass ampoule container suitable for volatile materials such as styrene. Typically 5.0 μl of styrene was sealed in the glass ampoule and then scanned at 5 degree/min from room temperature to 340°. The sample was then cooled in place and re-scanned to obtain a baseline for the heat of polymerization calculation. The energy measurement sensitivity of the DSC was calibrated using a small indium metal standard in a glass ampoule containing 5.0 μl ethyl benzene to better simulate actual experimental conditions of the styrene analysis.

Specific heat measurements were also run on the Dupont DSC unit.

Results and discussion

The thermal polymerization of styrene monomer inhibited with 10–15 ppm *t*-butyl catechol, was examined using the Accelerating Rate Calorimeter. The data plots obtained from the first experiment are illustrated in Figs 3 and 4. Under the experimental conditions, the temperature *vs.* time plot shows that the thermal polymerization of the monomer was detected at about 95° and that the heat

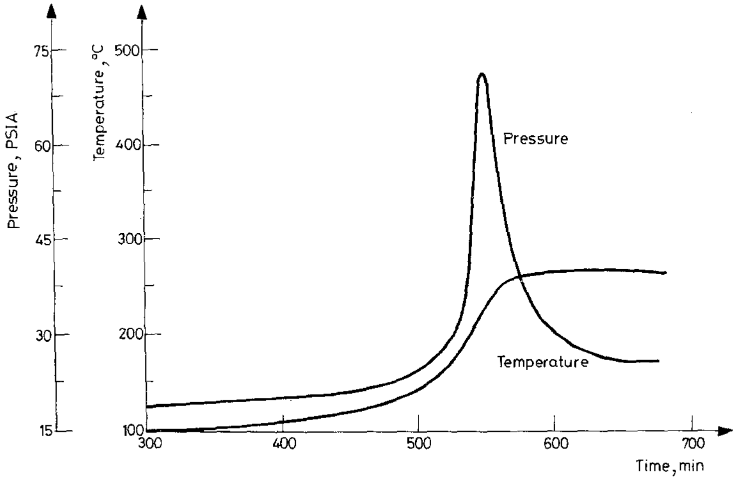

Fig. 3

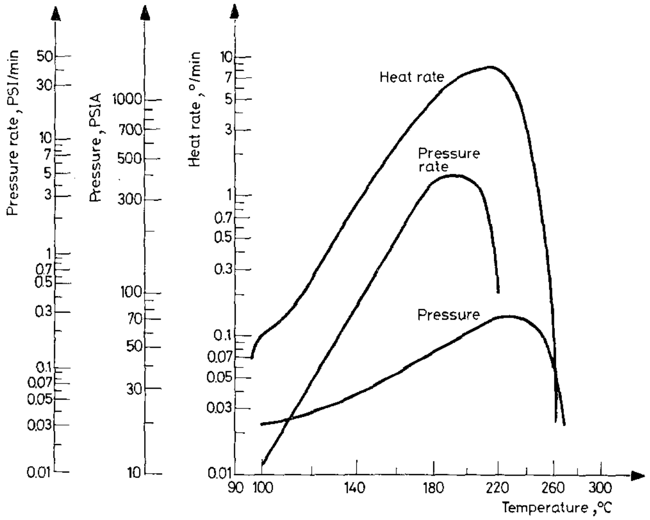

Fig. 4

Figs 3&4. Data plots from ARC experiment on inhibited styrene monomer, 4.74 g styrene, 9.47 g titanium bomb, air atmosphere, 50 °C start temperature, 5 °C heat-step interval, 15 minutes wait-time generated caused the temperature of the styrene and container to increase to 260° where the reaction was apparently complete. Figure 4 indicates that the self-heating rate of the sample/container system reached a maximum of 8.0 degree/min at 210°. Since pressure build-up in a closed vessel is an important parameter associated with runaway reactions, plots containing pressure data are also available from the ARC processor. Figures 3 and 4 also illustrate some of the various forms in which the pressure data may be plotted using the ARC.

The adiabaticity of the sample during the ARC experiment is an important parameter that one must take into account before applying ARC data to a specific problem. The adiabaticity of the sample at any time is defined in Eq. 1 as the portion of the heat of reaction being retained by the chemical, $q_{\mathrm{s,t}}$, divided by the total amount of heat being generated by the sample, $q_{\mathrm{T,t}}$.

$$\alpha = \frac{q_{\mathrm{s,t}}}{q_{\mathrm{T,t}}} \tag{1}$$

For reactions where a thermal steady-state exists at all times between sample and container, i.e. temperature gradients are constant or small, the heat being produced by the sample will be partitioned according to the heat capacities of the sample and container as defined by Eq. 2.

$$\Phi = \frac{M_{\mathrm{s}} C_{\mathrm{vs}} + M_{\mathrm{b}} C_{\mathrm{vb}}}{M_{\mathrm{s}} C_{\mathrm{vs}}} \tag{2}$$

where M_{s} and M_{b} are the masses of the sample and container or "bomb", respectively, and C_{vs} and C_{vb} are the specific heats of the sample and container at constant volume, respectively. Φ, or thermal inertia, is thus a special case of sample adiabaticity and is related to α according to Eq. 3 under conditions of thermal steady-state.

$$\Phi = \frac{1}{\alpha} \tag{3}$$

Although under the stated assumption of thermal steady-state both α and Φ are independent of time, they are still temperature dependent in most cases and C_{vs} is both temperature and composition dependent since in most reactions a change in heat capacity occurs as the reactant forms product.

Under conditions where thermal steady-state does not exist between sample and container, such as when the rate of heat produced by the sample is faster than the rate of heat transferred from sample to container, the problem becomes even more complex and one must use Eq. 1 directly since the sample adiabaticity will be a function of the rate of reaction and the heat transfer between the sample and the container besides the temperature and composition dependence of the heat capacities of the components in the system. Treating ARC data which were obtained under conditions of non-constant sample adiabaticity is difficult and beyond the scope of this paper.

Since the data of Figs 3 and 4 were obtained within the operating range of the ARC, 25° to 500° and 0.02°/min to 10°/min, it is reasonable to assume that near thermal equilibrium conditions existed during the experiment, and that average heat capacities can be used adequately to represent the sample and bomb. These data can now be applied to two hypothetical examples where the adiabaticities of the examples are chosen to be the same as that of the experimental data. This is done so that the ARC data can be applied directly to the example without further adjustments of the data. First, one must calculate the adiabaticity of the ARC experiment of Figs 3 and 4 using the specific heats of styrene monomer, polymer, and the container materials. Figure 5 contains specific heat data on both styrene and polystyrene [10, 11]. The specific heat of liquid styrene monomer above 100° is extrapolated from data acquired at lower temperatures because above this temperature the heat generated from the polymerization reaction interferes with the measurement. In contrast, the specific heat of polystyrene has been measured experimentally over a wide temperature range by many workers [11]. The specific heats of various sample container materials were measured in this laboratory by Differential Scanning Calorimetry (DSC) and are shown in Fig. 6.

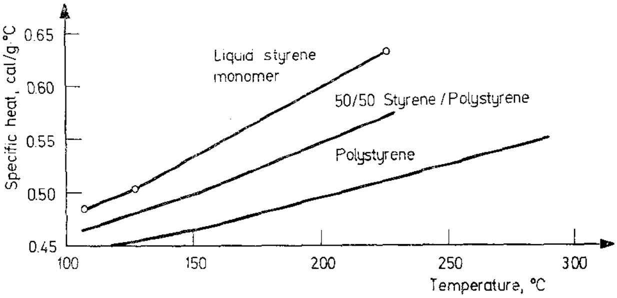

Fig. 5. Specific heat as a function of temperature of styrene (10), polystyrene (11), and the estimated average specific heat of a 50/50 mixture by weight of styrene and polystyrene

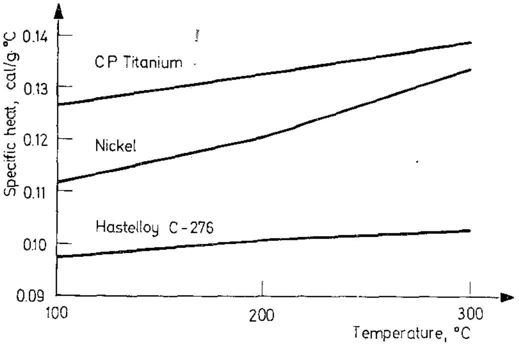

Fig. 6. Specific heat as a function of temperature for three ARC bomb materials as measured by DSC

The runaway polymerization depicted in Figs 3 and 4 covered a temperature range from 95° to over 260°. The average temperature, $T_{av} = T_0 + (T_0 + T_{f,s})/2$, for that particular experiment is half-way between the initial, T_0, and final, $T_{f,s}$, temperatures, or 178°. At this average temperature, the specific heat of styrene monomer is estimated as 0.57 cal/g.°C, that of polystyrene is 0.48 cal/g.°C, and that of commercially pure titanium is 0.132 cal/g.°C. At the average temperature of the reaction one can assume that approximately half of the styrene has reacted to form polymer and that a 50/50 mixture would exhibit a specific heat which would be the average of the specific heats of the monomer and polymer at that temperature, 0.53 cal/g.°C. It must be realized that linearly interpolating specific heat data while assuming a 50/50 mixture of monomer and polymer will introduce some errors into the calculation of Φ. A more rigorous approach is possible but is beyond the scope of this paper.

Since the masses of the styrene, 4.74 g, and the container, 9.47 g, are known, the average adiabaticity can be calculated. For the experiment represented in Figs 3 and 4, $\alpha = 0.67$ and $\Phi = 1.50$. This means that under these experimental conditions, on the average, the sample of styrene was 67% adiabatic with 33% of the heat generated from the reaction consumed in heating up the titanium container. Now consider the application of the data of Figs 3 and 4 to several examples.

The first case involves a laboratory which routinely runs tests on the rates of polymerization of styrene in small bottles in an oven which can be set at various temperatures. The typical sample size is 10 g (M_s) styrene of average specific heat 0.5 cal/g.°C (C_{vs} at 125°) in a bottle weighing 12.5 g (M_b) of average specific heat 0.2 cal/g.°C (C_{vb} at 125°). According to Eqs 2 and 3, $\Phi = 1.5$ for this example which is approximately the same as that of the data of Figs 3 and 4. Since the ARC under similar adiabatic (Φ) conditions detected an exothermic reaction above 95°, one might expect that if the laboratory runs its test near or above 95° (under conditions where little or no heat is lost from the bottle) an exothermic runaway reaction could occur in $\sim$ 4 hours, as indicated in Fig. 3, resulting in a pressure increase in the bottle. If the bottle was not constructed to withstand that pressure increase, the container would rupture.

Another example of how one might utilize ARC data would be a situation involving a distillation recovery system operating at 90 to 100° in a vessel rated for 25 psig with $\Phi = 1.5$ for the vessel, the same as for Figs 3 and 4. The data indicate that loss of cooling to the condenser could result in a polymerization runaway in the vessel. In addition, if after loss of cooling the vessel were purged with nitrogen to minimize flammability of the styrene but the vessel was inadvertently valved off so that it was closed, these conditions would be similar to those of the ARC experiment and one can see from the ARC pressure data that the runaway reaction could generate internal pressures in the vicinity of 70 psia in $\sim$ 4 hs. The pressure is well above the rated pressure for the vessel.

One should not be misled into thinking that the 70 psia maximum pressure observed in the ARC experiment of Figs 3 and 4 is the highest pressure ever possible during a thermal runaway polymerization of styrene. As will be shown later, rates of reaction, rates of pressure increase, maximum temperatures, maximum pressures, and times to maximum rate are all highly dependent on the sample adiabaticity and other factors. It will be shown that pressures much higher than 70 psia are possible during styrene polymerizations in the ARC under more adiabatic conditions.

In the examples presented thus far, care has been taken in using ARC data which was acquired under conditions of sample adiabaticity similar to the adiabaticity of the styrene in the example, i.e. $\Phi = 1.5$ for the small bottles of styrene in the laboratory and for the distillation column. It is important to understand the implicit assumption made in applying ARC data to industrial problems where the calculated adiabaticities are equivalent. The assumption is that the chemical and physical properties of the small ARC system accurately represent or simulate the large-scale industrial system. For ARC data to be accurate, the sample/container system must be near thermal equilibrium during the course of reaction which means data must be acquired between 0.02 degree/min and 5 to 10 degree/min self-heat rate. For the ARC data to be a reliable representation of a large scale distillation column, the distillation column and contents must also be near thermal equilibrium at all times. If there is no agitation in the liquid in the still then the assumption that thermal equilibrium exists may not be valid. Heat generated in a large distillation column of styrene may not transfer to the vessel very quickly resulting in a much more adiabatic runaway reaction in the still than that observed in the ARC. The ARC experiment would not be conservative. Another factor which can greatly affect the applicability of ARC data to a large-scale system is the change in heat transfer properties of the polymerizing monomer. At low conversions, early in the runaway reaction, the sample is mostly styrene with little polymer present. This material would exhibit a relatively high thermal conductivity along with a low viscosity which favors free convective heat and mass transfer when the material develops any temperature gradients during a runaway reaction. As the styrene polymerizes, however, the thermal conductivity of the system decreases while the viscosity increases which makes the transfer of heat from the liquid to its container more difficult. Thus, the polymerizing system may become more adiabatic as the reaction proceeds. This self-insulating tendency may result in a variable adiabaticity during the runaway in a large-scale system and would indicate that ARC data at $\Phi = 1.5$ do not simulate that part of the runaway where the sample adiabaticity increases or Φ decreases toward a value of 1.0 or perfect adiabaticity.

As another example of how ARC data can be used, suppose one would like to carry out a thermally initiated batch polymerization of styrene at 110°. The rate of reaction and the rate of heat generation can be estimated at 110° from the ARC data. If one can assume that the observed temperature rise is proportional to the conversion of monomer to polymer which assumes that the specific heat of the sample is independent of temperature, then the following equation can be written.

$$C = \frac{T_{\mathrm{f,s}} - T}{\Delta T_{\mathrm{AB,s}}} C_0 \tag{4}$$

Equation 4 relates the temperature of the ARC reaction profile to the concentration of monomer remaining at a given temperature in the exothermic runaway reaction where C is the concentration at any temperature T, C_0 is the initial concentration, $T_{f,s}$ is the final temperature of the reaction, and $\Delta T_{AB,s}$ is the observed experimental temperature rise which is calculated from Eq. 5, where T_0 is the initial temperature or the temperature at which the reaction was first detected in the ARC.

$$\Delta T_{AB,s} = T_{f,s} - T_0 \tag{5}$$

Differentiating Eq. 4 with respect to time and rearranging gives Eq. 6 which can be used to estimate the rate of polymerization at 110°. The fraction reacted is represented by x.

$$dx/dt = \frac{-dC/dt}{C_0} = \frac{dT/dt}{\Delta T_{AB,s}} \tag{6}$$

The above equation does not account for the reaction rate dependence on concentration changes during the experiment or reaction order effects and, therefore, should only be applied under conditions of negligible concentration depletion near the initial temperature, T_0. At 110° the styrene is approximately 9% polymerized for the reaction shown in Fig. 4.

Since $\Delta T_{AB,s} = 165°$ and $dT/dt = 0.13$ degree/min at 110°, the rate of reaction is approximately 4.7% per hour. This value is in close agreement with Platt's value of 4.5% per hour for initial rate of the polymerization of styrene at 110° [12]. The initial rate of heat generation at 110°, $\dot{q}_{110}$, can also be calculated from the ARC data according to Eq. 7.

$$\dot{q} = C_{v,s}\,\Phi \frac{dT}{dt} \tag{7}$$

Using Eqs 2, 3 and 7 along with the specific heats at 110°, $C_{vs} = 0.48$ cal/g.°C and$C_{vb} = 0.13$ cal/g.°C, the estimated rate of heat generation at 110° is 0.11 cal/g. min. It should be realized that these calculations of initial rates of polymerization and initial rates of heat evolution are only approximate and only apply to the early part of the reaction where percent conversion is low. This approach is not applicable to other portions of the ARC runaway curve except where the chemistry and kinetics of the reaction are known since the ARC data are dependent on degree of conversion. This technique is also limited to reactions that are not complicated by changes in mechanism early in the reaction such as autocatalytic processes.

In order to demonstrate the effect of operating temperature on a runaway polymerization, consider the same batch reactor discussed earlier, $\Phi = 1.5$, but now operating at 150° instead of 110°. Figures 7 and 8 show the corresponding ARC data for an experiment where the styrene sample was heated rapidly to 150° and then allowed to thermally runaway. In general, one can see from a direct comparison of Figs 3 and 4 to Figs 7 and 8 that allowing a runaway polymerization

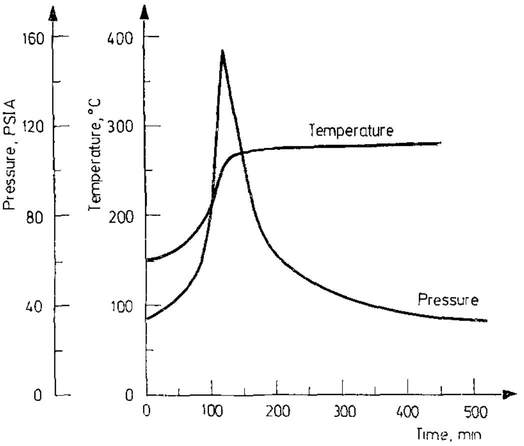

Fig. 7

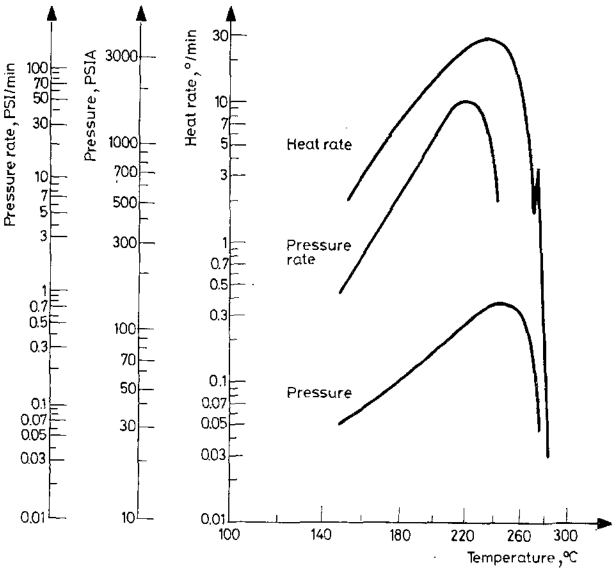

Fig. 8

Figs 7 & 8. Data plots from ARC experiment on inhibited styrene monomer with 150 °C start temperature, 4.74 g styrene, 8.83 g titanium bomb, air atmosphere

to start at a higher temperature shows substantial changes in the ARC data and that the latter case is the more severe from a hazards point of view. The final temperature observed was higher. The heat rates were higher at all temperatures with the maximum self-heat rate being a factor of three higher and the temperature of the maximum self-heat rate being 20° higher also. The maximum pressure observed was roughly double that of the 110° experiment. Probably the most dramatic difference between the two sets of data has to do with the pressure rates. The maximum pressure rate observed in the 150° experiment was 65 psia/min which is a factor of 11 greater than that of the 110° experiment. One should keep in mind that the quantitative application of these ARC data to the batch reactor operating at 150° may be unwise since the adiabaticity of the sample will probably be neither constant nor equal to that of the batch reactor under the high self-heat rate conditions observed by the ARC.

The polymerization of styrene involves a combination of initiation, propagation, and termination of the polymer chains formed during the reaction. However, for any commercially available styrene, one must also consider the effect of inhibitor on the polymerization. The presence of inhibitor is readily seen in the self-heat rate plot of Fig. 4. There is a very rapid rise in the self-heat rate when the polymerization reaction is first detected at 95°. The inhibitor prevents the polymerization by consuming the free radicals formed in the styrene. The production of free radicals in the styrene is temperature dependent with more radicals being formed as the temperature is increased. As free radicals are formed they are consumed by the inhibitor until the inhibitor concentration becomes so low that it can no longer effectively terminate the free radically initiated polymerization process. The ARC can be operated in the isothermal mode to gain more information on the effectiveness of the inhibitor. Suppose one wished to distill styrene at 80° in order to remove the inhibitor from the monomer prior to processing the material. How long would one have to correct an operating problem if a fresh batch of inhibited styrene was heated to 80° but could not be distilled immediately? Figures 9 and 10 illustrate the runaway polymerization data acquired after isothermally aging the styrene in the ARC at 80° under an air atmosphere for approximately 400 minutes. In terms of the stability of the inhibitor, one can now predict that under similar conditions the inhibited styrene can be held for 400 minutes at 80° before the inhibitor is consumed and polymerization of the styrene is detected. As far as the distillation operation is concerned, one can assume that after 4 or 5 hours at 80° that the risk of experiencing a runaway polymerization becomes quite high. In comparing the data from the isothermal age experiment to the data of Figs 3 and 4 one can readily see that the runaway appears to be less severe when the polymerization is allowed to begin a 80° rather than at 95°. The self-heat rates, the pressure rates, and the maximum pressure and temperature observed are all lower in the isothermal aging test.

It has been shown above that the presence of inhibitor can drastically change the interpretation of any thermal data for hazard evaluation. At first glance, the data shown in Figs 3 and 4 indicated that no thermal runaway reaction was observed at 80° and one might conclude that no risk exists at that temperature. However, the isothermal aging test of Fig. 9 showed that a runaway can occur at 80° if active inhibitor is lost. Presumably, at lower temperatures it would take longer to consume the inhibitor but if left indefinitely, the inhibitor would eventually be consumed and the polymerization reaction would begin to generate heat.

An important point about instrument sensitivity should be made. Unfortunately, it is common to refer to the initial temperature as the temperature at which the

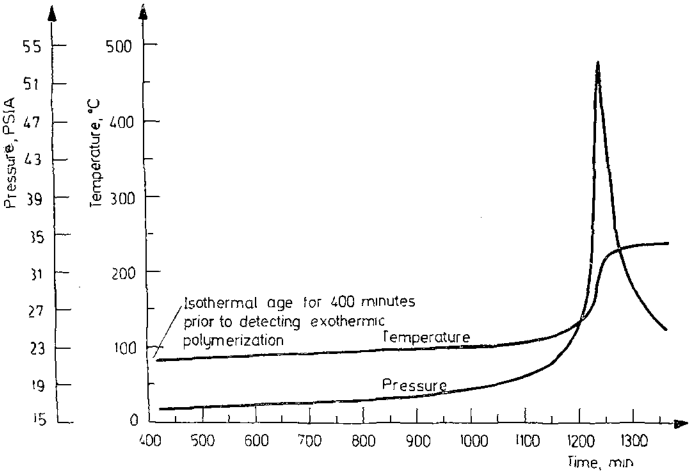

Fig. 9

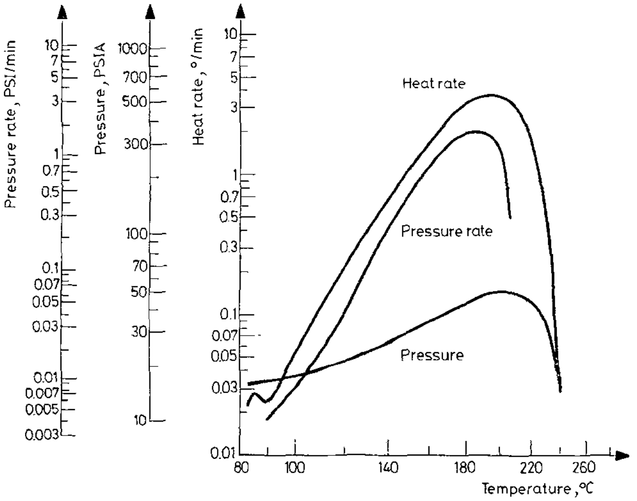

Fig. 10

Figs 9 & 10. Data plots from 80 °C isothermal age ARC experiment, 4.78 g styrene, 10.01 g titanium bomb, air atmosphere

exotherm "starts". This is rarely true chemically. What is usually meant is that the ARC, or any other thermal instrument, "detected" the exothermic reaction at the initial temperature. Uninhibited styrene will polymerize at 50° over several days time, but the rate of heat generation is so slow that the ARC cannot detect the reaction at that temperature. The self-heating rate may be on the order of 0.001°/min while the normal detection threshold for the ARC is 0.02 °/min. Thus, the reaction would go undetected at 50° in the ARC. This question of instrument sensitivity may be of little consequence for an uninsulated one-liter beaker of styrene at 50°, since heat losses to the environment should prevent any accumulation of heat accompanied by a temperature increase. However, ignoring the problem could easily be catastrophic for a 50 000 gallon storage tank where due to a relatively small surface to volume ratio heat is easily accumulated which could result in a runaway polymerization. It becomes a question of the rate of heat generated versus the rate of heat lost to the environment. If the rate of heat lost is always greater than the rate of heat generated by the reaction, then a thermal runaway will not occur. However, a runaway will occur if the reverse is the case.

As mentioned earlier, sample adiabaticity affects the self-heat rates, the pressure rates, maximum temperatures and pressures during an ARC experiment. Since Φ is related to sample adiabaticity under thermal equilibrium conditions, it is an indication of how much heat is taken from the sample to heat up the container in the ARC test. It is a thermal sensitivity factor which can be used to advantage. For very energetic reactions such as the thermal decomposition of highly energetic materials a large Φ will lower the observed final temperature, self-heat rates, and pressure rates. In this way the reaction rates can be kept within the instrument capabilities. In contrast, for a material which has a small heat of reaction, one might want to use a low Φ in order to obtain the largest temperature rise possible and to obtain as much thermal data as possible in the normal operating range of the instrument. There are other uses for varying Φ. Occasionally, for complex chemical systems, there are several possible parallel reactions which may differ in their kinetics. An ARC experiment with a low Φ may yield a self-heat rate curve which is quite normal in appearance but which may be concealing these

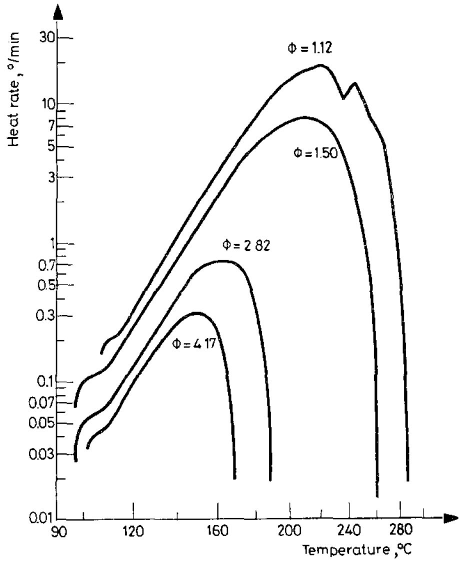

Fig. 11

multiple reactions. By increasing Φ, attenuating the self-heat rates, and repeating the analysis the previously hidden reactions can often be detected as well-resolved multiple reactions.

In order to see the effect of Φ on the ARC data, several experiments on styrene were carried out under varying conditions of Φ. Figure 11 compares four heat rate curves for styrene where the calculated Φ values varied from 1.12 for the nickel

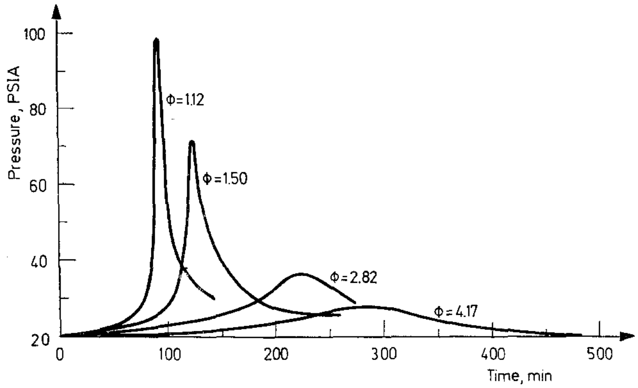

Fig. 12

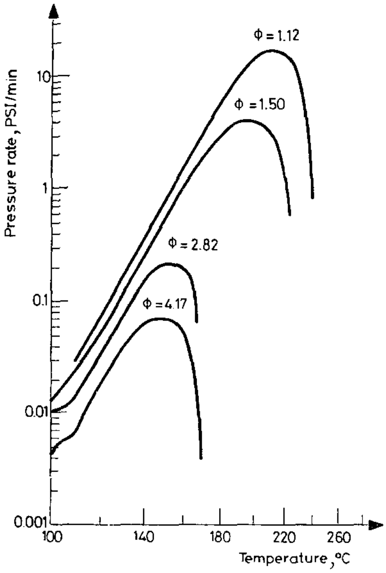

Fig. 13

Figs 11, 12 & 13. Comparison among ARC experiments on inhibited styrene run under different conditions of Φ. Heavy-weight Hastelloy C-276 bomb with $\Phi = 4.17$. Heavy-weight titanium bomb with $\Phi = 2.82$. Light-weight titanium bomb with $\Phi = 1.50$. Light-weight nickel bomb with $\Phi = 1.12$. All tests were run under air atmosphere, 50 °C start temperature, 5 °C heat-step interval, 15 minute wait-time container to 4.17 for the heavy-weight Hastelloy C container. As one can see from Fig. 11, a change in Φ from 4.17 to 1.12, a factor of 3.7, results in a seventyfold increase in the maximum self-heat rate, from 0.3°/min to 20°/min, respectively. The increase in self-heat rate as Φ decreases is dependent on the activation energy or the temperature sensitivity of the material of interest. For example, peroxides and high explosives typically have higher activation energies than that of styrene polymerization. Previous work on di-*t*-butyl peroxide showed that a factor of 2.8 decrease in Φ resulted in a 300-fold increase in the maximum self-heat rate observed in the ARC [9]. The effects of varying Φ on the pressures and pressure rates during a thermal runaway polymerization are shown in Figs 12 and 13. In this case the maximum pressure increased from 28 psia to 98 psia while the maximum pressure rate increased from 0.08 psia/min to nearly 20 psia/min when Φ is varied from 4.17 to 1.12, respectively. All the above arguments pertaining to the effect of Φ on runaway reaction data from the ARC also apply in general, but not necessarily quantitatively, to large-scale equipment, and must, therefore, be carefully considered for accurate scale-up of processes.

The adiabatic temperature rise that the sample container system underwent during the ARC experiment can be calculated from the observed initial, T_0, and final, T_f, temperatures according to Eq. 5. This temperature rise represents the energy involved in the polymerization of styrene under the stated experimental conditions. To calculate the temperature rise for a totally adiabatic runaway ΔT_{AB} where no heat is lost to the container one can correct $\Delta T_{AB,s}$ by using the estimated average Φ for the experiment and Eq. 8 and that there would not be any change in the reaction chemistry at the higher temperatures.

$$\Delta T_{AB} = \Phi \Delta T_{AB,s} \tag{8}$$

The energy of polymerization can be estimated from this adiabatic temperature rise for styrene according to Eq. 9, where Q_v is the heat measured due to polymerization.

$$\Delta E_v = Q_v = C_{v,s} \Delta T_{AB} \tag{9}$$

By combining Eqs 8 and 9 one arrives at a more condensed form, Eq. 10.

$$\Delta E_v = \frac{M_s C_{vs} + M_b C_{vb}}{M_s} \Delta T_{AB,s} \tag{10}$$

Since $\Delta(PV)$ is small compared to ΔE_v for these ARC experiments on styrene, then change in the enthalpy will be essentially the same as the change in energy, Eq. 11.

$$\Delta H_v = \Delta E_v + \Delta(PV) \sim \Delta E_v \tag{11}$$

If one can also assume that the average heat capacity of a 50/50 mixture of styrene and polystyrene is approximately linear with temperature then the heat of polymerization can be calculated for the average temperature of the ARC experiment.

The results are listed in Table 1. According to Stull [13], the heat of polymerization of liquid styrene monomer to 100 percent solid polystyrene is −73.6 to −74.9 kJ/mole between 120 and 200°. Typical ARC results lie below these values.

In order to discover the source of this discrepancy, several experiments were carried out. First, the polymerized styrene sample from the ARC was examined by gel permeation chromatography (GPC) to obtain the molecular weight distribution of the polymer, Fig. 14. When compared to a polystyrene standard, Fig. 15, which was thermally initiated and polymerized at much lower temperatures than those seen in the ARC, it is apparent that under runaway polymerization conditions, there is a tendency to form a lower molecular weight polymer. Data were not obtained on the ARC sample below 4000 molecular weight by this GPC method. Since there is a tendency to form a low molecular weight polymer during an ARC test, then there is the possibility that residual monomer, dimer, trimer,

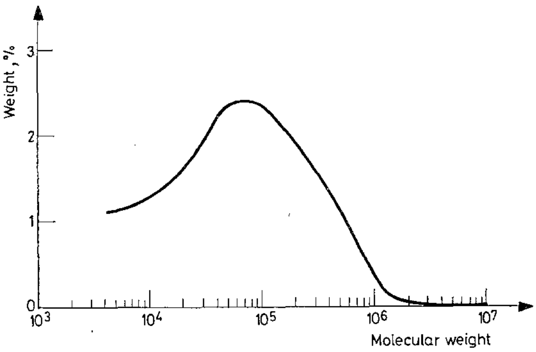

Fig. 14. Molecular weight distribution of polystyrene generated during thermal runaway of styrene in a light-weight titanium bomb

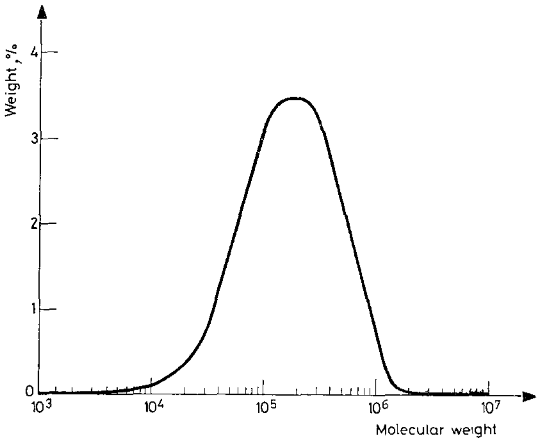

Fig. 15. Molecular weight distribution of a polystyrene standard

or tetramer could significantly lower the observed heat of polymerization of styrene in the ARC. A gas chromatographic analysis indicated that styrene monomer, dimer, and trimer species amount to only 3% of the polystyrene sample from the ARC. This small amount of incomplete polymerization cannot be the sole cause of the low heats of polymerization listed in Table 1.

Table 1

Calculated heat of polymerization of styrene monomer by ARC

Bomb	Average temperature T_{av}, °C,	Φ at T_{av}	$\Delta T_{AB,s}$ °C	ΔH at T_{av} experimental, kJ/mole	ΔH at T_{av}, D. R. Stull [10] kJ/mole
Heavy-weight Hastelloy C-276	135	4.17	68	−60.5	−73.6
Heavy-weight Titanium	144	2.82	93	−56.2	−74.4
Light-weight Titanium	179	1.50	166	−57.5	−74.7
Light-weight Nickel	197	1.12	193*	−51.3*	−75.1

* Due to the high self-heat rates observed during this experiment, $\Delta T_{AB,s}$ was corrected according to the procedure outlined in the ARC operator's manual [14].

The ARC data were next compared to data obtained by a special differential scanning calorimetric (DSC) method designed for reactive volatile materials [2]. This technique utilizes a small sealed glass ampoule as the sample container. The scan-rate and sample size were selected so that the exothermic polymerization was forced to occur over a slightly wider temperature range, 100 to 340° than that over which the ARC data were acquired. This was done to approximate the dynamic nature of the temperature during the ARC experiment. After the DSC experiment reached 340° the sample was cooled in place and the baseline scanned. A typical DSC trace of styrene with baseline scan is illustrated in Fig. 16. The average heat of polymerization observed by this DSC approach was −69.8 kJ/mole with a range of ±3.3 kJ/mole for three runs, which is consistent with the literature value [18]. The expected reproducibility of this DSC technique is ±14% at

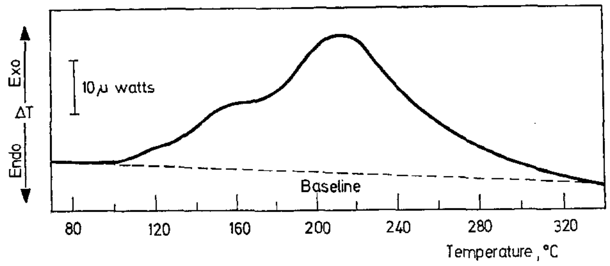

Fig. 16. DSC curve of the polymerization of inhibited styrene monomer in a sealed glass ampoule. Baseline was rescanned after the polymerization reaction was complete. 5 degree/min scan-rate, 5.0 μl sample

the 95% confidence level. Analysis for residual monomer, dimers, and trimers were not carried out on these samples. These DSC results suggest that the cause of low heats of polymerization of styrene in the ARC may be instrumental in origin.

One possible heat loss path in the ARC is the conduction of heat up the bomb stem to the pressure feed-through adapter attached to the nickel-plated copper lid. In order to minimize any heat losses via this pathway, a light-weight titanium bomb was loaded with styrene and the bomb stem sealed mechanically. The bomb was suspended in the calorimeter chamber by a thin wire and the measurement thermocouple was attached. The observed heat of polymerization for that experiment was −56.8 kJ/mole indicating that heat losses up the bomb stem are not the cause of the low values. Heat losses could occur by way of conduction, convection, and radiation in the air filled ARC calorimeter chamber.

The only item in the calorimeter chamber which does not have active temperature control during an exothermic reaction is the radiant heater assembly. Therefore, with the radiant heater removed, the jacket heaters were used to raise the temperature of a styrene sample to about 80° where it was isothermally aged until the polymerization was detected and followed adiabatically to completion as in a normal ARC experiment. The observed heats of reaction were more exothermic in all cases listed in Table 2. Tests on di-*t*-butyl peroxide in toluene indicate that

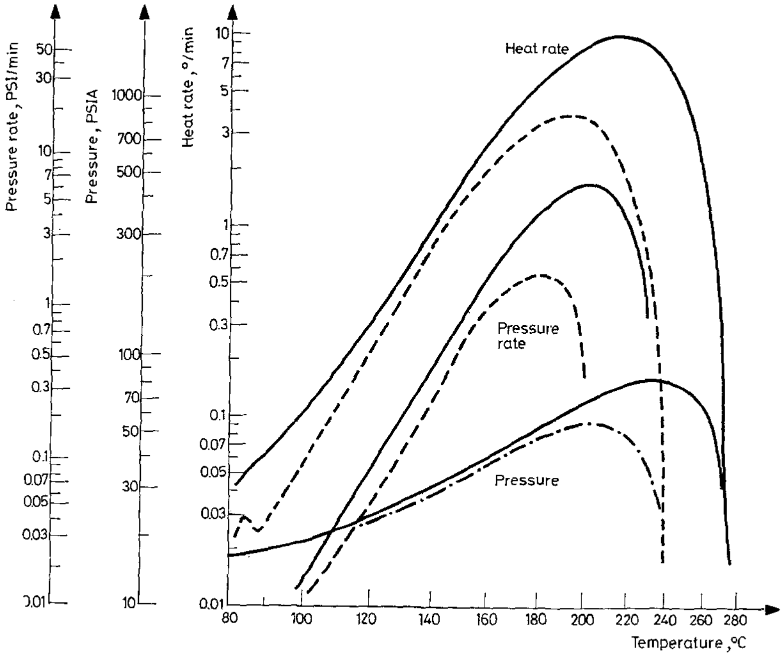

Fig. 17. Effect of radiant heater assembly on ARC data, $\Phi = 1.5$, ——— no radiant heater present, (– – –, – · – · –) standard radiant heater assembly utilized

Table 2

Calculated heat of polymerization of styrene monomer by ARC without a radiant heater assembly

Sample container	Φ 4.33	$-\Delta H_{\mathrm{ARC}}$, kJ/mole	Relative error between $-\Delta H_{\mathrm{ARC}}$ and ΔH_{DSC}, %	Relative error between $-\Delta H_{\mathrm{ARC}}$ and $-\Delta H_{\mathrm{Literature}}$ [10], %
Heavy-weight Hastelloy C-276	4.33	61.3	−13	−17
Heavy-weight Titanium	2.86	66.4	−5	−11
Light-weight Hastelloy C-276	1.79	66.9	−4	−10
Light-weight Titanium	1.47	65.7	−6	−12
Light-weight Nickel	1.12*	62.8*	−10	−16

* Due to the high self-heat rates observed during this experiment, $\Delta T_{\mathrm{AB,s}}$ was corrected for heat losses according to the procedure outlined in the ARC operator's manual [14].

the heat lost to the radiant heater assembly is negligible for that chemical system when examined in the ARC with the maximum rate occurring between 1 and 10 degree/min. Since theperoxide decomposition is a high activation energy process compared to the polymerization of styrene, it is suspected that heat losses to the radiant heater assembly only become evident during slow reactions of relatively low activation energy where heat loss effects can accumulate over wide temperature ranges and long periods of time. Research is currently underway to minimize these effects and thereby further extend the lower limit of the instrument.

The removal of the radiant heater assembly affects the ARC reaction rate data. Two experiments run under similar experimental conditions, $\Phi = 1.50$, are compared in Fig. 17. In one experiment the radiant heater was removed while in the other the standard radiant heater assembly was employed. The data illustrate how the presence of the radiant heater, presumably resulting from energy losses during the early part of the reaction, lowers the self-heat rates throughout the experiment. For this case of long reaction times at low self-heat rates, significant energy losses also affect both pressures and pressure rates, probably due to increased conversions at lower temperatures causing a lowering of the data maxima. From these data it is clear that the effect of the radiant heater should be taken into account when treating ARC data in a quantitative manner. Alternatively, the experiment could be designed to avoid the slow portion of the reaction.

The results listed in Table 2 show that when the radiant heater assembly has been removed from the instrument, the ARC and DSC results are in good agreement for the heat of reaction. Both ARC and DSC results are from 5 to 10% less exothermic than literature sources would predict. These differences may be due to the many assumptions made in treating the experimental data, in the uncertainties in the specific heats and heats of reaction obtained from the literature, or from as yet unknown experimental problems.

*

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Notation

α	sample adiabaticity
$q_{s,t}$	heat retention rate of sample
$q_{T,t}$	total rate of heat generation of sample
M_s	sample mass
M_b	sample container mass
C_{vs}	specific heat of sample at constant volume
C_{vb}	specific heat of sample container at constant volume
Φ	thermal inertia
T_0	initial temperature of exotherm
$T_{f,s}$	final temperature of exotherm

T_{av}	average temperature during exotherm
$\Delta T_{AB,s}$	experimental temperature rise
ΔT_{AB}	adiabatic temperature rise of sample
ΔE_v	change in internal energy at constant volume
Q_v	total heat generated by sample at constant volume
ΔH_v	change in enthalpy at constant volume
P	pressure
V	volume
C	concentration
C_0	initial concentration
x	fraction reacted

ZUSAMMENFASSUNG — Die thermische Polymerisation eines gehemmten Styrolmonomers wurde durch Accelerating Rate Calorimetry (ARC) untersucht. Die durch diese Technik erhaltenen Zeit-Temperatur-Druck-Daten wurden zur Bewertung der mit der industriellen Herstellung von Styrolmonomeren verbundenen thermischen Gefahren verwendet. Mehrere Beispiele über Deutung und Einsatz von ARC-Daten unter Laboratoriums- bis zu Versuchsbetriebsbedingungen werden gegeben, einschließlich Erörterungen hinsichtlich der Ähnlichkeiten und Unterschiede zwischen ARC und betriebsgemäßen Vorrichtungen. Die Polymerisation des Styrolmonomers wird auch zur Bewertung der Leistung von ARC in einem weiten Temperaturbereich, von 80 bis 300° eingesetzt. Die Daten zeigen, daß die Entfernung der Strahlungsheizvorrichtung eine bessere Übereinstimmung zwischen den durch ARC gemessenen und in der Literatur vorhandenen Werten der Polymerisationswärme von Styrol ergibt. Es wird angenommen, daß dieser Effekt nur unter Bedingungen niedriger Reaktionsgeschwindigkeiten während längerer Zeiträume, wie im Falle des Styrolmonomers, beobachtet werden kann.

Резюме — С помощью калориметрии с возростающей скоростью исследована термическая полимеризация ингибированного стирола. Полученные этим методом данные время-температура-давление, использованы для определения факторов термической опасности при промышленной переработке стирола. Представлено несколько примеров интерпретации и применения этого метода в окружающей обстановке от лабораторных условий до промышленных масштабов, включая обсуждение подобий и различий между оборудованием для калориметрии с возростающей скоростью и крупномасштабным оборудованием. Полимеризация стирола использована для оценки действенности этого метода в области температур 80—300°. Опыты показали, что удаление источника теплового излучения приводит к лучшему согласию между теплотой полимеризации стирола, измеренной этим методом и соответствующими литературными данными. Считается, что этот эффект будет наблюдаем только для случая низких констант скоростей в течении длительного периода времени, как это имеет место в случае стирола.