

# METHOD FOR EXTRACTING ARRHENIUS PARAMETERS FROM TRANSIENT TEMPERATURE EXPERIMENTS

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Reactions described by first order Arrhenius kinetic models require estimates of two parameters: the frequency factor,  $A$  ( $s^{-1}$ ), and activation energy,  $E$  (J/mole) which must be determined experimentally. The governing function is transcendental, complicating the process. Classically one measures the rate at which products are formed or the rate at which reactants disappear as a function of temperature in constant temperature experiments. Transient temperature experiments with varying yields present a new level of difficulty, since the elaborate curve fitting required often masks the underlying kinetic processes. This is especially true in Microwave Assisted Chemistry (MAC) since it is never possible or practical to achieve constant temperatures. Further, in some cases, it may not be possible to directly measure the rate of product evolution or reactant disappearance; rather the experiment yield is the only quantity that may be measured. These experiments are difficult in that they consist of a single end-point assessment of the yield with transient  $T(t)$  records, and classical Arrhenius plots in that case are nearly useless.

I describe a new method of experimental analysis which makes recorded transient  $T(t)$  curves analyzable on standard Arrhenius axes. Briefly, Arrhenius integrals are calculated for measured  $T(t)$  curves with a wide range of assumed values for  $A$  and  $E$ . The  $A$ - $E$  plane is searched for sets of values which give the measured yield, which invariably lie along a straight line. In the  $A$ - $E$  plane the intercept gives the time and slope gives the temperature of an equivalent constant temperature experiment with the same yield. The equivalent constant temperature experiment conditions are then plotted on standard Arrhenius axes to estimate  $A$  and  $E$ . The method is designed for single end-point experiments, but may be used equally well with data in which the disappearance of reactants is measured in real time during a transient exposure. The method is tested in synthetic processes, first and second order, and on data from decay of fluorescence in AT-1 tumor cells.