1. Foundation and definitions

a. Chemical models for kerogen decomposition

The formation of hydrocarbon molecules from a large kerogen molecule must somehow involve cleavage of chemical bonds, leading to both liberation of small oil and gas molecules and alteration of the residual kerogen structure. Cleavage of chemical bonds can in principle occur via two distinct types of pathways: simple unimolecular decomposition, in which the bond in question is stretched enough to eventually break; and multi-center reactions, in which two or more moieties within the molecule interact, allowing old bonds to break simultaneous with formation of new bonds. Although multi-center reactions can certainly occur, it seems to us unwise to assume that the majority of petroleum-forming reactions occur via complex mechanisms that require highly specific molecular aggregations, geometries, and structures.

Finally, although we intuitively think of hydrocarbon molecules as being formed directly from a moiety of a kerogen molecule, they can also be formed via stable chain reactions. The series of equations in Figure 1 below describe one common type of chain reaction. Chain reactions consist of at least three steps: a unimolecular initiation reaction that creates a reactive intermediate; two or more reactions (unimolecular or bimolecular collisions between the intermediate and a reactant molecule) that propagate the intermediate; and a bimolecular termination reaction that destroys the intermediate, ending the chain.

\[
\begin{align*}
\text{Initiation (}\alpha\text{)} & : R \rightarrow I_1 \\
\text{First propagation (}\beta\text{)} & : I_1 + R \rightarrow I_2 + P_1 \\
\text{Second propagation (}\gamma\text{)} & : I_2 \rightarrow I_1 + P_2 \\
\text{Termination (}\delta\text{)} & : 2I_1 \rightarrow P_3 
\end{align*}
\]

Figure 1. Schematic chain reaction showing the initiation step (\(\alpha\)), two propagation steps (\(\beta\) and \(\gamma\)) and a termination step (\(\delta\)) for a reaction that produces three products (\(P_1, P_2,\) and \(P_3\)). \(R\) is the original reactant and \(I_1\) and \(I_2\) are intermediates (e.g., Rice and Herzfeld, 1934; Lewan, 1998b). Side reactions may result in formation of additional intermediates and products.
b. Kinetic parameters and reaction order
Simple decompositions are unimolecular processes that follow first-order kinetics – that is, the rate of decomposition depends linearly on the concentration \([S]\) of the reacting species \(S\):

\[
\text{Rate} = k[S]
\]  

where \(k\) is the reaction rate constant for loss of \(S\). The value of the rate constant \(k\) varies with absolute temperature \((T)\), and is defined by the Arrhenius equation (2), which in turn is controlled by the Arrhenius constant \(A\) (also called the A factor), as well as by the activation energy \((E_a)\):

\[
k = A \exp(-E_a/RT)
\]

where \(R\) is the gas constant.

c. Chain reactions
The overall kinetic expression for a chain reaction can be much different. It depends upon the particular reaction sequence, but the apparent overall order for a chain process is commonly fractional (e.g., 3/2), rather than first order, because of the algebra involved in computing the kinetic parameters for multistep processes. The values for the apparent activation energy and apparent frequency factor for chain reactions can also be quite different than those for simple decompositions. A factors for bimolecular reactions of molecules are mainly between \(10^{10}\) and \(10^{12}\) \(s^{-1}\) (Benson, 1976, p. 148), while those for bimolecular reactions of radicals (as we might find in the propagation step) are typically between \(10^8\) and \(10^9\) \(s^{-1}\) (Benson, 1976, p. 157). Since the apparent \(A\) factors for chain reactions depend on the \(A\) factors for the various steps in the chain \(
A_{cr} = A_{\beta}^{n}(A_{\alpha}/(2A_{\delta}))^{0.5}
\) for the reaction in Figure W2), we anticipate \(A\) factors of about \(10^{11}\) \(s^{-1}\) for hydrocarbon generation via a chain reaction. The fact that \(A\) factors of this magnitude are almost never reported for laboratory simulations of hydrocarbon generation suggests that chain reactions are not dominant in that process.

d. Choosing between simple and chain processes
In addition to the theoretical analysis in the preceding paragraph, we can use the experimental data themselves to empirically derive a reaction order, and hence a mechanism. Conventionally, the order of a hydrocarbon-degradation reaction is established by plotting the rate constants determined from isothermal pyrolysis experiments against heating times of variable duration. If the data can be adequately fit by a first-order equation, that fact is generally considered sufficient evidence that the reaction is unimolecular, and hence first order. In the course of much experimental work it has generally been possible to fit laboratory data for hydrocarbon generation to first-order kinetics, suggesting again that simple decomposition is of greater importance than chain reactions.

However, various authors have demonstrated problems with this method of determining reaction order (e.g., Dominé et al., 1998). If wide ranges of temperature and time are used experimentally, the observed relationship between \(k\) and time is not always perfectly linear. The higher reaction temperatures used in the laboratory compared to those in sedimentary basins may cause different reactions to be rate limiting in high- and low-temperature systems. For instance, Dominé (1991)
noted during pyrolysis of n-hexane -- a chain-reaction sequence where decomposition and hydrogen transfer reactions constituted the main portion of the chain -- that hydrogen-transfer reactions were rate limiting at lower temperatures, while decomposition reactions became rate limiting at higher temperatures. The change in dominance of different reactions with varying temperature can perturb the relationship between k and heating time/rate. There is thus a risk that a reaction that appears to be first order at laboratory temperatures may not actually be first order at geological temperatures.

e. Parallel reaction model
The process of hydrocarbon generation, whether by simple decomposition or via a chain reaction, comprises many different simultaneous reactions. These reactions can involve breaking different types of bonds, or breaking the same types of bonds within a slightly different environment within the kerogen structure. When we speak of the rate of oil generation, or gas generation, or hydrocarbon generation, we are therefore speaking of the sum of the rates of numerous individual reactions, each of which generates a certain type of hydrocarbon molecule from a specific part of a kerogen molecule. Equation (1) thus becomes

\[ \text{Rate} = k_1[S_1] + k_2[S_2] + \ldots + k_n[S_n] \]  

where the \( k_1 \) is the rate constant for the first reaction and \([S_n]\) is the concentration of the nth and final reactive species. Since we cannot know all the details for all possible reactions, we simplify our model by grouping the reactions into a manageable number of categories -- typically fewer than 20.

f. Constraints from thermodynamics
The value of the Arrhenius factor \( A \) is controlled by the entropy of activation (\( \Delta S^\ddagger \)) of the reaction, where \( \Delta S^\ddagger \) represents the change in freedom that occurs in going from the ground state of the reacting moiety to the transition state (Benson 1976). For unimolecular reactions it is inevitable that \( \Delta S^\ddagger \) will be positive, since the stretching of the to-be-broken bond in moving from ground state to the transition state will always lead to an increase in the ability of the individual atoms to vibrate and rotate freely. From statistical mechanics, Benson (p. 86) calculates that if \( \Delta S^\ddagger = 0 \), at a reaction temperature of 600K, the value for \( A \) for a unimolecular decomposition reaction will be \( 10^{13.55} \text{ s}^{-1} \). At a more typical temperature for oil generation of 135°C (408K), \( A = 10^{13.38} \text{ s}^{-1} \). Since \( \Delta S^\ddagger \) will normally be considerably greater than zero, we can be confident that the value of \( A \) for the great majority of reactions involved in hydrocarbon generation is greater than \( 10^{13.38} \text{ s}^{-1} \). See Waples (1996) for a lengthier discussion.

g. Empirical data
Empirical data for the reactions of chemical compounds (Benson, p. 98) provide an upper limit for the value of \( A \). Excluding two anomalies, the measured values of \( A \) range from \( 10^{14.8} \) to \( 10^{17.5} \text{ s}^{-1} \), with a mean near \( 10^{16} \text{ s}^{-1} \). If we want to describe all the reactions involved in the transformation of kerogen to hydrocarbons using a single typical \( A \) factor, that \( A \) factor will surely fall between the absolute minimum of \( 10^{13.38} \text{ s}^{-1} \) and \( 10^{16} \text{ s}^{-1} \). Tang et al. (1996) and Zhang et al. (2008) have also suggested that \( A \) should fall between \( 10^{11} \) and \( 10^{16} \text{ s}^{-1} \).
The range of published A factors for source rocks (Fig. 2) overlaps well with the range for pure chemicals compiled by Benson. The published A factors were all determined automatically by data-reduction software, with median and mean values of $2.9 \times 10^{14}$ s$^{-1}$ and $2.5 \times 10^{14}$ s$^{-1}$, respectively. We interpret those data to support our hypothesis that A should be near $2 \times 10^{14}$ s$^{-1}$.

![Figure 2. Logs of A factors shown in histogram form for hydrocarbon-generation kinetics published for 259 source rocks. All these A factors were determined by allowing both A and Ea to vary freely during derivation of kinetic parameters from raw pyrolysis data.](image)

**h. Activation-energy distribution**

Each of the terms in equation (3) represents a distinct group of chemical reactions. Substituting equation (2) into equation (3), we have, at any temperature T,

$$
\text{Rate} = A_1 \exp(-Ea_1/RT)[S_1] + A_2 \exp(-Ea_2/RT)[S_2] + \ldots + A_n \exp(-Ea_n/RT)[S_n] \quad (4)
$$

where the relative abundances of the reacting species within the kerogen structure are variable. The individual reactions bundled into each group may differ in chemistry, but their activation energies are always similar. From group to group, however, activation energies vary systematically. We thus speak of an “activation-energy distribution”, where each member (group of reactions) in the distribution is defined by its activation energy, and the relative proportion of each group $[S_i]$ is also specified. Today the great majority of applications use a standard spacing of 1 kcal/mole between groups (that is, $Ea_{i+1} = Ea_i + 1.0$ kcal/mole: Figure 3). Some groups, however, especially the French Petroleum Institute, have used wider spacing. In fact, the earliest
pseudokinetic models (Tissot, 1969; Deroo et al., 1969) used 10-kcal spacing, which changed to 5-kcal spacing (Ungerer, 1984), before the IFP settled in 1986 on 2-kcal spacing (e.g., Ungerer et al., 1986; Tissot et al., 1987; Ungerer and Pelet, 1987; Espitalié et al., 1988). Other groups besides the IFP have occasionally used spacing greater than 1 kcal (e.g., Issler and Snowdon, 1990; Min et al., 2011). Sundararaman et al. (1992), however, showed that 2-kcal spacing could be inadequate, and advocated 1-kcal spacing.

By convention, we normally simplify the analysis by assuming today that the A factors for all activation energies for each kerogen are the same (e.g., Ungerer and Pelet, 1987). This assumption is supported by Benson (1976, pp. 90-104), who showed that for typical unimolecular decomposition reactions A decreases very slightly as temperature increases over the narrow range of temperatures involved in hydrocarbon generation (a range of less than 100°C). However, Benson’s data also indicate that A increases very slightly as Ea increases. During natural heating, these two effects effectively cancel, lending support to our assumption of constant A for all activation energies in an Ea distribution (see also Waples, 1996). Pseudokinetic models and the earliest true-kinetic models, in contrast, generally assumed that A increased as Ea increased (e.g., Tissot, 1969; Deroo et al., 1969; Ungerer, 1984). More recently, Min et al. (2011) have also allowed A to vary, although their A values do not change regularly with Ea.

![Figure 3. Activation-energy distribution for the Mae Sot kerogen from onshore Thailand, with a spacing of 1 kcal/mole between groups. A = 4.5*10^{12} s^{-1}. From Tegelaar and Noble, 1994.](image-url)
g. Summary
Activation-energy distributions with a 1-kcal/mole spacing provide a simple, convenient, and useful model for hydrocarbon generation from kerogen. Wider spacing of Ea values does not provide the precision required by modern applications of kinetics. Narrower spacing may be useful for Type I kerogens with very narrow Ea distributions.

Combining the various types of relevant data, we conclude that a single A factor of $2 \times 10^{14}$ s$^{-1}$ can be defended and used effectively in calculating hydrocarbon generation from all kerogens. This value is slightly higher than the A factor of $1 \times 10^{14}$ s$^{-1}$ previously suggested by Waples et al. (2002, 2010). We do not feel that using different A factors for different kerogens, or different A factors for different activation energies in the Ea distribution, improves accuracy or convenience in applications of source-rock kinetics. Kinetics with A factors below about $1 \times 10^{14}$ s$^{-1}$ or above about $4 \times 10^{14}$ s$^{-1}$ (e.g., Fig. B) should either be converted to kinetics with an acceptable A factor, or else not used.

2. Historical perspective
   a. Kinetics prior to 1987
      i. Kinetics from pyrolysis of coals and oil shales
      The earliest kinetic descriptions of hydrocarbon generation came from studies of the pyrolysis of coals and oil shales (see Waples, 1984, for a detailed review). Those studies were interested in commercial retorting, however, and gave no thought to using kinetics to model hydrocarbon generation under geologic conditions. Therefore, their empirical data apply only to high-temperature processes, and are of no direct interest for petroleum exploration. In fact, as Deroo et al. (1969) and Waples (1984) pointed out, these mathematical descriptions were widely recognized even at that time as “pseudokinetics” rather than true kinetics.

      The early pseudokinetics all used a single activation energy, rather than a distribution. Jüntgen and Klein (1975) and Tissot and Espitalié (1975) were the first to note that hydrocarbon generation, a process that consists of many parallel reactions, could be described either by a distribution of activation energies, or by a single pseudoactivation energy and pseudo-A factor that were very different from any of the activation energies or A factors in the true distribution.

      ii. Earliest activation-energy distributions
      The earliest published activation-energy distributions were those of Tissot and his colleagues (Tissot, 1969; Deroo et al., 1969). By modern standards they were simply pseudokinetics, using activation energies and A factors that no one would care to defend today. In retrospect, however, they represented a revolutionary step forward, although it would take nearly two decades for those early efforts to evolve into something closely resembling modern source-rock kinetics.

      iii. TTI method
      The TTI method, developed by Lopatin (1971) and popularized by Waples (1980), is a quasi-kinetic method of calculating hydrocarbon generation. In the pre-computer era it allowed development of interest in modeling hydrocarbon generation, but its technical limitations became apparent to many workers during the 1980’s (e.g., Quigley and Mackenzie, 1988), and by the early 1990’s it had been almost entirely replaced by the kinetic models discussed later in this
chapter (Waples, 1996). Although the TTI method is mainly of historic interest today, in its day it represented an extremely important advance in geochemistry, and provided a platform and driving force for the development of modern basin modeling.

b. Kinetics since 1986
From approximately 1986 onward (e.g., Ungerer et al., 1986; Tissot et al., 1987), all source-rock kinetics that have been published and widely used closely resemble the kinetics we use today. These kinetics are generally considered to be true kinetics rather than pseudokinetics. The reactions involved in petroleum formation, and the kinetics that describe those processes, can be presented in several different formats, as described below.

i. Number of hydrocarbon products
1. One product (total hydrocarbons)
Most available kinetic parameters represent generation of “hydrocarbons” and do not distinguish oil generation from gas generation. The reason for this simplification is purely practical: it is much faster and much less expensive to derive kinetics for total hydrocarbons than to generate different kinetics for different products. If, as is usually the case, we want to model oil generation and gas generation, the total hydrocarbons are simply broken down into the desired products in pre-specified proportions. The kinetic parameters are taken to be the same for generation of all products. Consequently, in such schemes oil and gas are generated simultaneously, and the gas-oil ratio does not vary during the entire hydrocarbon-generation process.

2. Two products (oil, gas)
Separate kinetics have occasionally been measured for oil generation and gas generation (e.g., Espitalié et al., 1988; Braun et al., 1992; Pepper and Corvi, 1995b). These data support the idea that oil generation largely precedes gas generation (Fig. 4). However, cost has prevented routine measurement of separate kinetics for oil and gas.

However, Waples and Mahadir Ramly (2001) have shown that published data depicting the general relationship between the kinetics of gas generation and kinetics of oil generation can be used to estimate how total-hydrocarbon kinetics can be divided mathematically into separate kinetics for the two products. Although this method is inexact, it is inexpensive and does provide results that are consistent with published information, such as that shown in Figure 4.
Figure 4. Generation of oil and gas from the Type IIb (marine clastic) kerogen published by Espitalié et al. (1988) using separate oil and gas kinetics at a constant heating rate of 3°C per million years.

3. Multiple products
It is also possible to measure kinetics on a larger number of products (e.g., Espitalié et al., 1988; Braun et al., 1992; Dieckmann et al., 1998, 2000). Most commonly, oil is divided into normal oil and light oil (or heavy oil, medium oil, and light oil), while gas is divided into methane and wet gas. Some workers believe that the greater detail afforded by these subdivisions aids in economic evaluation of exploration opportunities. The largest disadvantage of these complex kinetic schemes is that the data necessary to use them can only be obtained by slow and very expensive analyses. Applications in exploration have therefore been sparse.

ii. Reaction schemes
Most kinetic formulations today assume that hydrocarbons are generated directly from kerogen in a single step:
Kerogen → Hydrocarbons \hspace{1cm} (5)

However, some workers prefer to a reaction scheme in which kerogen is transformed into bitumen, and the bitumen is then converted into hydrocarbons:

\[ \text{Kerogen} \rightarrow \text{Bitumen} \rightarrow \text{Hydrocarbons} \] \hspace{1cm} (6)

Bitumen is thus viewed as an intermediate product that is not expelled, and is therefore distinct from our desired products. Some of the earliest pseudokinetics (e.g., Deroo et al., 1969; Pelet, 1970) describe multi-step generation.

Although the formulations in equations (5) and (6) look different, they generally do not differ kinetically. When a chemical process consists of two or more sequential steps, it is virtually inevitable that one of the steps will be much slower than the other. This slow “rate-determining” step controls the rate and kinetics of the overall reaction; that is, a change in the rate of the faster step(s) does not affect the overall rate or the kinetics. We can therefore model both reaction schemes using the same kinetic equations, and the distinction between schemes (5) and (6) fades away.

More-complex schemes, often called reaction networks, have also been created that include a variety of interconversions and feedbacks (e.g., Braun and Burnham, 1992, 1993). For example, normal oil can decompose to smaller molecules, such as light oil, wet gas, and/or dry gas. In addition, the decomposition of the initial kerogen is sometimes assumed to produce not only hydrocarbons, but also an altered kerogen that is still capable of generating additional hydrocarbons, which are normally assumed to be smaller molecules than the products from the original kerogen. Such reaction schemes can quickly become exceedingly complex. Some of these complex schemes have fallen into disuse, while others survive today, albeit with limited applications.

iii. Activation-energy distribution

1. Discrete
The great majority of source-rock kinetics are reported as discrete activation-energy distributions with a spacing of 1 kcal between reaction groups (e.g., Fig. 3). Discrete $E_a$ distributions are the default option for the software used in deriving kinetics from source-rock pyrolysis data.

2. Gaussian
Pepper and Corvi (1995a, b) used Gaussian $E_a$ distributions rather than discrete ones to describe the kinetics they assigned to their organofacies. The Gaussian distributions are defined by two numbers: the mean activation-energy in the distribution, and the standard deviation of the distribution. (As the standard deviation increases, the distribution becomes broader.)

Gaussian activation-energy distributions are always symmetrical, a constraint that is at odds with the asymmetry found in many discrete distributions (e.g., Figure 3). Given that discrete distributions can be better fitted to most laboratory data, the use of Gaussian distributions seems to have no advantage.
iv. **Single activation energy**

Some discrete Ea distributions are very narrow (Fig. 5), but technically they are distributions because the data-analysis procedures would allow the creation of a distribution if one were necessary to fit the data. Some methods of determining source-rock kinetics, however, are not capable of creating Ea distributions (see later). Instead, they yield a single activation energy for the entire hydrocarbon-generation process. This result contradicts both the results obtained from other methods that are capable of generating Ea distributions, and the concept that kerogen decomposition occurs via many different pathways.

![Figure 5. Narrow Ea distribution derived from a homogeneous Type I kerogen (Ordovician-age Yeoman Formation, Williston Basin, Canada). From Burrus et al. (1996).](image)

v. **Non-first-order kinetics**

It has been noted that hydrocarbon generation from some kerogens cannot be fit well using first-order kinetics (e.g., Burnham et al., 1996). Those authors suggested that this failure represented a specific challenge to the parallel-reaction scheme for kerogens with a very narrow Ea distribution, and a more general challenge to our conceptual kinetic model. However, in unpublished studies we have found that a much better fit for narrow Ea distributions can be achieved by making two simple adjustments in the derivation of kinetic parameters: reduce the Ea spacing to less than 1 kcal/mole, and adjust the values of the individual activation energies to non-integers (e.g., the Ea distribution consists of a series of Ea groups such as 52.35, 52.85, 53.35, etc.). We therefore believe that first-order kinetics are adequate for modeling hydrocarbon generation from all source rocks.

3. **Determination of kinetics**

The three different methods of obtaining source-rock kinetics in the laboratory are discussed and described in the following sections.
a. **Rock-Eval®-type pyrolysis (anhydrous, open system)**

By far the most common method of measuring source-rock kinetics has been open-system, anhydrous pyrolysis using a Rock-Eval®, a Source Rock Analyzer®, or some similar instrument. The pyrolysis temperature is increased at a steady rate during pyrolysis, beginning at about 300°C and ending at about 550°C. Heating rates ranging from about 0.3°C to 60°C per minute have been used by various workers. Typical experimental conditions and procedures are described by Braun et al. (1991).

The pyrolysis data (time, temperature, hydrocarbon yield) are then subjected to mathematical analysis using one of the commercially available software programs designed to extract kinetic parameters (A and Ea distribution) from the pyrolysis data. The most common approach taken by the software has been to allow A and the Ea distribution both to vary freely, with the values selected by the software to achieve the best mathematical fit between measured pyrolysis yield and the pyrolysis yield predicted by the particular combination of A and Ea being tested. A historically less-popular option has been to fix the A factor and allow the software only to adjust the Ea distribution to achieve the fit.

Two alternative approaches have been used in acquiring kinetics from open-system pyrolysis experiments. The traditional approach has been to carry out multiple pyrolysis runs (typically three, but ranging from two to five) on each sample, at various heating rates. The objective is to measure pyrolysis yield as a function of time and temperature over as wide a range of thermal histories as possible. The reasoning behind this approach is that as equation (2) shows, the rate constant k (and hence the rate of hydrocarbon generation) depends linearly on A but exponentially on Ea. Therefore, by requiring a simultaneous fit at multiple heating rates, we can separate the effects of A and Ea, and thus determine the best kinetic parameters for each kerogen.

Attractive as this approach is, it was strongly criticized long ago by a number of workers (Nielsen and Dahl, 1991; Lakshmanan et al., 1991), who pointed out convincingly that the range of achievable laboratory heating rates is far too narrow to allow software to reliably separate the effects of A and Ea. The final A-Ea combination chosen by the software may indeed provide the absolute best mathematical fit, but the quality of that fit is not significantly better than a very large number of other fits that invoke widely variable combinations of A and Ea. This phenomenon is commonly called the “compensation effect”, since a change or error in A can be compensated by a change or error in Ea. The standard data-reduction method is thus able to identify a huge family of acceptable solutions, but cannot reliably pick the correct one. Unfortunately, this important criticism was universally ignored for over a decade by those who were generating kinetics data. (see also Stainforth, 2009).

The alternative method, first suggested by Waples (1996), and first applied systematically by Waples et al. (2002) and later by Waples et al. (2010), is to manually assign a value for A. The latter two studies used \( A = 1 \times 10^{14} \text{ s}^{-1} \), and justified that choice as consistent with the laws of thermodynamics, as explained at the beginning of this article. More recently, Waples (unpublished) has preferred \( A = 2 \times 10^{14} \text{ s}^{-1} \), on the basis of reconsideration of the thermodynamic arguments, as well as on the distribution of published A values determined by allowing A to vary freely (Fig. A). An additional justification for fixing A is that one can avoid really bad A-Ea combinations that are occasionally produced when A is allowed to vary freely. Erroneous A-Ea
combinations can cause serious problems in applications of kinetics in exploration, as discussed later. Finally, if one uses the same A value for all samples, it is easy to compare Ea distributions from different kerogens. In contrast, if A values for two kerogens are different, it is not quick and easy to compare the Ea distributions, or to know which kerogen will generate earlier.

By fixing A, we can determine the Ea distribution using only a single pyrolysis run made at a relatively fast heating rate, typically 25°C to 30°C per minute (Waples et al., 2002, 2010). Our unpublished tests have shown that one-run kinetics are identical to those obtained from multiple runs, provided that the A factor is fixed to the same value. One-run kinetics drastically lower the cost of each kinetic analysis, making it possible to acquire much larger data bases of source-rock kinetics. The larger data bases in turn make possible the applications of source-rock kinetics to organofacies analysis and as a thermal indicator, as discussed later in this article.

Finally, we find that performing a quick and inexpensive clean-up extraction prior to kinetic analysis will in some cases greatly improve the quality of the kinetics data. Extraction removes not only contamination from migrated oil or mud additives, but also bitumen, some of which comes out in the S2 peak and thus affects the kinetics. Even where contamination is not a major problem, extraction increases the confidence level in the results and simplifies interpretation.

b. Closed-system pyrolysis
   i. Hydrous pyrolysis

Hydrous pyrolysis (HP) is a closed-system technique that utilizes water and crushed organic-rich rock or kerogen isolate to simulate generation of hydrocarbons and expulsion of oil (Lewan et al., 1979; Lewan, 1985). In these experiments, water provides both a source of pressure and an exogenous source of hydrogen (e.g., Hoering, 1984; Lewan, 1997). In addition, water permits development of an immiscible oil phase (Lewan and Ruble, 2002). Typical experiments are carried out isothermally for about 72 hours at temperatures between 300°C and 360°C (Lewan, 1985; Lewan and Ruble, 2002).

HP experiments generate low amounts of alkenes, polars, and aromatic compounds, and greater amounts of paraffinic products than open-system anhydrous pyrolysis (e.g., Lewan et al., 1979). The greater compositional similarity between natural hydrocarbons and the products of HP is often interpreted as indicating that the chemical reactions taking place in HP systems are more similar to those taking place in nature, and thus that the kinetic parameters from HP studies should be more similar to those in natural systems. Complicating these interpretations is the fact that experimental conditions (heating time and temperature; reactor type, composition, and mass) can affect the type and amount of products generated (Lewan, 1993).

Calculation of Ea and A from HP experiments is quite different than from open-system pyrolysis. The hydrocarbon-generation sequence in an HP system is normally assumed to occur via two sequential reactions. The first of these reactions generates bitumen from kerogen in a relatively fast step that is followed by the slow rate-limiting step: generation of oil and gas from the intermediate bitumen. Kinetic parameters calculated from HP data are typically referenced to the expelled oil phase, and thus do not capture the full range of hydrocarbon molecules generated. A single activation energy (not a distribution, as in open-system pyrolysis) and a single value for A are then determined using a classic Arrhenius plot, which shows the log of the observed rate constant k (with respect to the immiscible oil phase) plotted versus the inverse of
the absolute temperature (Lewan, 1985). Calculation of kinetic parameters by this method assumes that the reactions being described are of first order. Because plots of k vs. time produced from HP experiments are consistent with a first-order reaction model, proponents believe that data from HP studies support the assumption that the rate-limiting step does in fact follow first-order kinetics (e.g., Lewan and Ruble, 2002).

Other workers, however, disagree with the derivation of kinetic parameters from HP experiments. In a discussion concerning Lewan’s (1997) work, Burnham (1998) criticized Lewan’s method of determining Ea and A. Lewan (1998a) responded to Burnham’s criticisms, objecting in turn to some of the assumptions of Burnham and other workers in deriving kinetic parameters from open-system studies. Although the intensity of the debate has subsided, the differences of opinion between the two camps have not been formally resolved.

Kinetic parameters derived from HP data have been used successfully in describing and predicting the extent of oil generation in a number of natural systems. Examples include Hunt et al. (1991), Ruble et al. (2001), Lewan (2002), and Lewan and Ruble (2002).

ii. MSSV pyrolysis

Another closed system technique that has been applied to understand petroleum generation is micro-scale sealed vessel (MSSV) pyrolysis. This method was originally devised by Horsfield et al. (1989) to use only milligram quantities of kerogen isolate. Glass beads and small aliquots of kerogen (20-50 mg) are packed into small MSSVs, capillary tubes with capacity of about 40 μL. The tubes are sealed at room temperature under anhydrous conditions and heated either isothermally or nonisothermally. Pyrolysate compositions are determined by gas chromatography (GC).

The MSSV technique allows compositional-kinetic models to be used, and kinetic parameters are calculated using mass-balance approaches and parallel-reaction models (e.g., Schenk and Horsfield, 1993). The extraction of kinetic parameters occurs in two steps: the cumulative hydrocarbon yields vs. temperature profiles from the raw data are smoothed with spline functions, and then those spline functions are differentiated to obtain the rate of hydrocarbon formation as a function of temperature (e.g., Schenk and Horsfield, 1993). Using the curves relating rates of hydrocarbon formation to temperature, kinetic parameters can be optimized by standard curve-fitting routines, after assuming a fixed number of parallel reactions and fixed spacing of activation energies.

Since calculating compositional kinetics directly from MSSV experiments can be time- and labor-intensive, shorter work flows for predicting hydrocarbon composition are sometimes applied (e.g., di Primio and Horsfield, 2006). The transformation ratio (TR) curve for a given kerogen will be determined by open-system anhydrous pyrolysis following the method developed by Pelet (1985). Non-isothermal MSSV experiments will then be conducted using multiple capillary tubes containing kerogen aliquots. To evaluate changes in product composition, tubes are cracked and analyzed by GC at multiple points along the temperature profile of the TR curve.

The rate of heating employed in pyrolysis experiments has a significant effect upon the proportion of different fractions (i.e., saturate/aromatic or saturate/unresolved compound ratios) in the MSSV product yields. This variation creates difficulty in producing accurate and
consistent compositional-kinetic models. It has been shown that this problem can be overcome by running a series of pyrolysis experiments on the same sample at different heating rates, and attempting to extrapolate compound proportions back to reasonable geologic heating rates (Dieckmann et al., 2000).

iii. Gold-tube reactor pyrolysis

Gold-tube reactor pyrolysis experiments are superficially similar to MSSV experiments. Slightly more material is used than in MSSV, with 50 to 500 mg generally employed. Both kerogen isolates (e.g., Behar et al., 1992; Behar et al., 1997) and liquid hydrocarbons (e.g., Behar and Vandenbroucke, 1996) have been investigated using this method.

Two main methods are used in these experiments to derive kinetic parameters. In some cases classic Arrhenius plots can be used (Behar and Vandenbroucke, 1996; Behar et al., 1997), while mathematical optimization is employed in others (Behar et al., 1992). Arrhenius plots are utilized to investigate individual hydrocarbon species (e.g., Behar and Vandenbroucke, 1996) or hydrocarbon mixtures containing “molecular tracers”, which are added chemical compounds whose kinetic behavior is well known (e.g., Behar et al., 1997). Mathematical optimization is utilized in experiments on complex hydrocarbon mixtures where the kinetic model is based around a detailed multi-reaction scheme in which each reaction is explicitly described.

Gold-tube pyrolysis experiments are used only infrequently to determine source-rock kinetics, mainly because of the expense involved in the experimental setup and the time and expertise required to produce consistent and reliable results.

c. Summary and recommendations

The main criticism of open-system pyrolysis is that the hydrocarbon products are demonstrably unlike the products of natural hydrocarbon generation. Most obviously, products produced in the laboratory contain many alkenes, whereas those formed under natural conditions contain none (e.g., Lewan, 1997). However, it has not been definitively shown that the kinetics of anhydrous open-system pyrolysis are different than those from hydrous pyrolysis. As Burnham (1998) has pointed out, many or all of the apparent differences result from the different methods of data analysis required by the different pyrolysis systems, and thus at this stage of our knowledge cannot be used as proof that one method is superior to others.

Kinetics derived from Rock-Eval®-type pyrolysis in a single run using a fixed A factor near 2*10^{14} s^{-1} yield very reasonable results in modeling studies or as thermal indicators (see next section). Given the low cost and rapid acquisition of those data, this method seems to have significant advantages over multiple-run Rock-Eval-type kinetics that allow A factors to vary freely. The method is also much more practical than closed-vessel pyrolysis methods.

4. Applications of source-rock kinetics

Source-rock kinetics can be applied in three different ways in petroleum exploration. Each of these applications is discussed in the following sections. Kinetics for a sample can be easily defined by the mean activation energy (Mean Ea) and the shape of the Ea distribution.

a. Basin modeling
The earliest, and for many years the only, application of source-rock kinetics was in basin modeling, in which kinetics were used to calculate hydrocarbon generation for a particular proposed thermal history. This application continues today, and will undoubtedly become even more important in the future, as basin modeling becomes more common in all phases of exploration. In addition, more-accurate kinetics resulting from A factors that are fixed to acceptable values will increase the accuracy and confidence in basin modeling, and thus promote even more of this type of work. Finally, since unconventional and hybrid plays assume little or no migration, a precise knowledge of levels of hydrocarbon generation at the prospect locations is much more important than in conventional exploration, where long-distance migration is often anticipated. Continuing interest in unconventional and hybrid exploration will thus utilize basin modeling more frequently than in the past.

Specific applications of source-rock kinetics in modeling include creating plots of oil and gas generation or Transformation Ratio through time for specific horizons of interest; and maps of Transformation Ratio or cumulative volumes of hydrocarbons generated for a specific horizon. Applications for conventional and unconventional exploration are both valuable, but are somewhat distinct, because the questions asked in the two exploration realms are different.

b. Organofacies analysis
The first application of source-rock kinetics to organofacies was by Waples et al. (2002), who identified distinct organofacies in Inner Ramp and Outer Ramp lithofacies of the Tithonian carbonate source rock of the southern Gulf of Mexico (Fig. 6). Other geochemical techniques had previously found no consistent difference between the two lithofacies.

![Figure 6. Different activation-energy distributions found for kerogens in the Inner Ramp lithofacies (left) compared to the Outer Ramp lithofacies (right) in the Tithonian of the southern Gulf of Mexico. A = $1 \times 10^{14}$ s$^{-1}$ for both kerogens. After Waples et al. (2002). Kinetics were also able to distinguish Ordovician strata rich in Gloeocapsamorpha prisca from those lean in G. prisca (Fig. 7). In both examples the distinction between organofacies is](image)
potentially important for exploration, since the different organofacies, with different kinetics, generate hydrocarbons at different times and temperatures.

![Figure 7. Different activation-energy distributions found for two samples from the same Ordovician source rock. Left: G. prisca-rich facies with high TOC, with dominant $E_a = 55$ kcal/mole. Right: G. prisca-lean facies with low TOC, with dominant $E_a = 54$ kcal/mole. $A = 1 \times 10^{14}$ s$^{-1}$ for both kerogens.](image)

Source-rock kinetics have also been used to aid in sequence-stratigraphic interpretation. Both the shapes of the $E_a$ distributions and the Mean $E_a$ values within the “F” Member of the Cenomanian-Santonian Abu Roash Formation of the Western Desert of Egypt correlate well with other basic source-rock parameters (e.g., TOC, Rock-Eval® S2, Hydrogen Index), and help show that the “F” Member (duration about 2 million years) represents a single sequence, and delineates the different system tracts within that sequence (Fig. 8).
c. Thermal indicator

It has long been known that Ea distributions change during maturity, as the weaker bonds in kerogen are broken faster than the strong bonds. Waples et al. (2002) were the first to quantify this phenomenon, using Mean Ea as an indicator of the progress of hydrocarbon generation (Fig. 9). It is possible to calculate the Transformation Ratio and the Ro equivalent for a sample if we know the Ea distribution for the immature kerogen (Waples et al., 2010) (Figs. 9 and 10). As Waples and Marzi (1998) noted, the relationship between Ro and TR is unique for each kerogen.
Figure 9. Activation-energy distributions for three samples from the sample organofacies, showing the change in shape of the Ea distribution as maturity increases from immature (top) to moderately mature in the middle to highly mature (bottom). Note also the increase in calculated Transformation Ratio (TR) and calculated Ro with increasing maturity.
Figure 10. For the immature kerogen at the top of Figure EA (top), plots of Transformation ratio (TR) vs. Mean Ea (top); Ro as a function of Mean Ea (middle) and Ro as a function of TR (bottom).
Once a relationship among Mean Ea, TR, and Ro has been established for a particular source rock, kerogen, or organofacies, those relationships can be used in several ways in hydrocarbon exploration. One application is to calibrate and improve geological models, since 1-D maturity modeling calculates Ro values that can be compared with those obtained from Mean Ea data. By changing the paleoheat flow or the amount of erosion at an unconformity, discrepancies between the modeled Ro values and those derived from measured Mean Ea values can be eliminated (Fig. 11), and our understanding of the geological history can be improved.

![Figure 11](image_url)

*Figure 11. Left: calculated Ro profile (gold line) assuming 1500 m erosion at the surface unconformity. Right: same profile calculated after reducing erosion to 600 m. Data (crosses) include Ro equivalents calculated from measured Mean Ea values for three samples from each of two different organofacies (A and B). Note that although Mean Ea for the two organofacies is different, the Ro equivalents are very similar.*

Mapping of maturities derived from source-rock kinetics can also be of great value in exploration. Figure 12 shows a color dot map of Transformation Ratio calculated from measured Mean Ea values in one source rock in numerous wells across a study area. Dot maps are ideal for presenting the geochemical data in a format that is both scientifically sound and visually impacting. In contrast, a valid contour map would have to take into consideration other geologic factors, such as present-day depth, amounts of erosion, present-day heat flow, and variations in paleoheat flow.

In this example, it is clear that the highest TR values are in the southeastern quadrant, and the lowest in the southwest, with a very steep and narrow transition zone between immature and highly mature. TR values in the northern part of the area, in contrast, are much less variable, and their distribution is less regular. Interpretation of these data in a full geologic context would be
challenging, but that challenge ultimately provides an opportunity to attain a deeper level of understanding, and to obtain thereby a competitive advantage, especially if this source rock is being examined as an unconventional target. Other similar maps, such as Ro equivalent or degree of expulsion, can also be created from the same Mean Ea data, and can be used for other purposes in the exploration process, including calibrating regional thermal history and providing the input for migration modeling.

Figure 12. Map of Transformation Ratio (values shown) calculated from Mean Ea values in one source rock across a basin. TR = 0 is shown in black. TR increases from purple through blue and green to yellow and red. See text for discussion.

5. Recommendations
We believe that kinetics that describe either total hydrocarbon generation, or generation of oil and gas as two distinct products, are suitable for the great majority of exploration applications. The quickest, least-expensive, and most-reliable method for determining total-hydrocarbon kinetics is to perform a single open-system pyrolysis run at a heating rate of about 25°C per minute, to fix the A factor to a reasonable value during the derivation of the kinetic parameters, and to use a spacing of 1 kcal/mole or less in the activation-energy distribution. Separate kinetics for oil generation and gas generation can then be estimated using existing data as a template. Although imperfect, this method for dividing total-hydrocarbon kinetics into oil and gas kinetics is inexpensive and appears to be reasonably reliable.

If one wants to have kinetics for more than two hydrocarbon products, those kinetics currently must be determined using a completely different technology that is much slower and more
expensive, factors that greatly limit the applicability of this approach. Kinetics for large numbers of hydrocarbon products are mainly applied where an extremely detailed picture of hydrocarbon composition is required. Different workers have quite different opinions about the cost/value relationship of this amount of detail.

Regardless of which type of kinetic scheme is used, A factors should be between $1 \times 10^{14}$ s$^{-1}$ and $4 \times 10^{14}$ s$^{-1}$ in order to yield satisfactory results when applied at geologic heating rates.

Utilization of the one-run method for determining kinetics lowers the cost per sample, and thus permits the acquisition of much larger data bases of source-rock kinetics. These larger data bases not only provide internal quality controls, but also permit the application of source-rock kinetics in two important new ways, in addition to the traditional application for calculating hydrocarbon generation during basin modeling: as an indicator of organofacies, and as an indicator of both thermal history and the progress of hydrocarbon generation. We strongly recommend the routine application of source-rock kinetics in all three ways for conventional, unconventional, and hybrid plays.

6. References


