

**BAYESIAN MODELLING TO PREDICT CHEMICAL KINETICS****Technical Field**

[0001] The present disclosure relates to the use of Bayesian modeling to predict chemical kinetics.

**Background**

[0002] Chemical kinetics, also known as reaction kinetics, is a branch of physical chemistry concerned with understanding rates of chemical reactions and/or chemical phase changes. Changes in heat flow or mass are used to measure reactions and/or phase changes for various chemicals. Conventional measurements may only be capable of assessing reactions and/or phase changes after collection of complete data, such as a complete thermogram. The time scales involved in such data acquisition range from seconds to days depending on the system involved and the kinetic regime that is interrogated, which can be particularly time consuming when screening the temperature range of interest without any prior knowledge, as is the case in an unknown sample.

[0003] Such problems may be defined thermodynamically, but many systems are still experimentally studied in such slow regimes because of rapid changes in the mechanism at temperatures closer to the event, low-energy systems that have small phase change or reaction enthalpies, or other cases where application conditions dictate the desired temperature range for measurements. Changes in mechanism at temperatures of slow kinetics may be particularly important for extrapolation in shelf-life or stability measurements, phase changing materials, catalysts with high activation energies, and/or large rate constants. Some instruments also may have slower instrument response times, which constrains the fastest event they can measure.

**Summary of the Disclosure**

[0004] The present disclosure relates to the use of Bayesian modeling to predict chemical kinetics. A measurement of chemical kinetics over a period of time can be initiated. Data collected from the measurement can be modeled recursively, via Bayesian modeling, to an expected rate of change of the chemical kinetics over a period of time thereby yielding a predicted rate of change of the chemical kinetics over the period of time before completion of the measurement over the entirety of the period of time. Values of empirical parameters of an

equation describing the chemical kinetics can be predicted recursively based on the predicted rate of change of the chemical kinetics over the period of time before completion of the measurement over the entirety of the period of time. A probability of the predicted values can be calculated recursively before completion of the measurement over the entirety of the period of time. A peak in the predicted rate of change over the period of time can be predicted and a probability of the peak can be calculated recursively before completion of the measurement over the entirety of the period of time. The measurement can be stopped before completion thereof over the entirety of the period of time in response to the probability being greater than a threshold value.

[0005] Embodiments described herein can allow prediction of values of empirical parameters of an equation describing the chemical kinetics and/or a peak in a rate of change of chemical kinetics over a period of time during acquisition of the data and the use of incomplete data to make decisions (automated or otherwise) in a laboratory or chemical plant process. Such techniques can be useful to make such predictions without having to measure data at all points of the period of time, thereby saving time and expense. The time savings can be significant, particularly in the cases of low-temperature, slow kinetic, or high-throughput systems. The measurement can be aborted when the model confidence is deemed sufficiently high that prediction of the parameters of interest will not change with the acquisition of further data.

[0006] The above summary of the present disclosure is not intended to describe each disclosed embodiment or every implementation of the present disclosure. The description that follows more particularly exemplifies illustrative embodiments. In several places throughout the application, guidance is provided through lists of examples, which can be used in various combinations. In each instance, the recited list serves only as a representative group and should not be interpreted as an exclusive list.

#### **Brief Description of the Drawings**

[0007] Figure 1 is a prior art graph of a rate of change of chemical kinetics over a period of time.

[0008] Figure 2A is a graph of a posterior predicted rate of change of chemical kinetics over time after measurement at two data points for a first example experiment.

[0009] Figure 2B is a graph of a posterior predicted rate of change of chemical kinetics over time after measurement at six data points for the first example experiment.

[0010] Figure 3 is a graph of the percent standard deviation in the prediction of the rate of change of chemical kinetics versus the number of data points collected for an example experiment.

[0011] Figure 4A is a graph of a posterior predicted rate of change of chemical kinetics over time after measurement at two data points for a second example experiment.

[0012] Figure 4B is a graph of a posterior predicted rate of change of chemical kinetics over time after measurement at twenty-three data points for the second example experiment.

[0013] Figure 5 is a block diagram of a system for Bayesian modeling to predict chemical kinetics.

[0014] Figure 6 is a block diagram illustrating an example of a method for Bayesian modeling to predict chemical kinetics.

[0015] Figure 7 is a block diagram of a machine within which a set of instructions, for causing the machine to perform various methodologies discussed herein, can be executed.

### **Detailed Description**

[0016] The present disclosure relates to the use of Bayesian modeling to predict chemical kinetics. More specifically, the present disclosure relates to the use of Bayesian modeling to predict a rate of change of chemical kinetics over a period of time. The chemical kinetics being measured can correspond to rates of chemical reactions and/or chemical phase changes, such as crystallization, melting, degradation, curing, oxidation induction, sorption, desorption, material stability, and/or reaction profiles, among others. Chemical kinetics includes investigations of how experimental conditions influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that also can describe the characteristics of a chemical reaction.

[0017] Calorimetry is the science or act of measuring changes in state parameters of a sample for the purpose of deriving the heat transfer associated with changes of its state due, for example, to chemical reactions, physical changes, or phase transitions under specified constraints. A non-limiting example of calorimetry is differential scanning calorimetry, which is a thermoanalytical technique in which the difference in the amount of heat required to increase

the temperature of a sample and reference is measured as a function of temperature. Differential scanning calorimetry can be used to measure characteristic properties of a sample, such as fusion and crystallization events, glass transition temperatures, oxidation, and other chemical reactions. Such techniques can be used for quality testing and research. Embodiments are not limited to a particular type of calorimetry. Polymeric materials can be examined to determine their thermal transitions such as glass transition temperature, crystallization temperature, and melting temperature. Polymer degradation can be shown by the lowering of the expected melting temperature and/or by oxidative onset temperature/time.

**[0018]** Changes in heat flow or mass are used to measure reactions and/or phase changes for various chemicals. These include crystallization and melting of semicrystalline polymers and other materials, reaction and curing profiles of liquids and solids, material stability assessment (e.g., shelf life oxidative stability), and sorption and desorption onto surfaces or into bulk material. Such processes can obey equations describing the chemical kinetics, which can be used to track their extent and rate during the measurement. However, conventional measurements may only assess this after the collection of complete thermograms, which can require significant amounts of time to acquire.

**[0019]** Figure 1 is a prior art graph of a rate of change of chemical kinetics over a period of time. The horizontal axis indicates time 104 (e.g., step time between measurements) in minutes over which the data points in the graph were collected. The vertical axis indicates a value of the measured chemical kinetics 102, which in this example is heat flow. The heat flow is normalized for sample mass, where  $Q$  represents the net heat transfer in watts per gram (W/g). Each of the plots shown is for the same sample at different temperatures. The peaks are well established by the ten minute mark. However, data was collected through the ninety minute mark. Arguably, the points to the right of the ten-to-twenty minute marks may not have been necessary, particularly if the goal was to determine the peaks. In chemical processing and the chemical industry, wasted time is expensive. In the case of temperatures close to different chemical or physical phenomena, wasted time may lead to a convolution of kinetics.

**[0020]** At least one embodiment described herein addresses the above and other deficiencies by using Bayesian modeling to accelerate the collection of calorimetry data and to make decisions based thereon more efficiently. Bayesian modeling can be used to predict the position of a peak, predict the value of empirical parameters in equations describing the chemical

kinetics, and/or to extract useful parameters from a thermogram without operator input. Any such prediction can be used to make decisions (automated or otherwise) in high-throughput analytical measurements or a reactive chemical event. Chemical producers use calorimetry in quality control, analytical, and high-throughput labs to make decisions about product acceptability and to solve problems.

**[0021]** Some previous approaches may use machine learning to improve the efficiency and reproducibility of data analysis by automating manual tasks that are time consuming for high volume data sets or prone to human error and/or to facilitate the interpretation of complex thermograms with convoluted peaks or peaks that are difficult to fit. However, such approaches are limited to assessing trends and statistically significant differences, extracting thermodynamic parameters (e.g., enthalpy of phase transitions, enthalpy of binding, entropy, etc.), and improving the accuracy of peak fitting. Such approaches are not aimed at stopping the measurement early, but instead are aimed at modeling all of the data once captured. Such previous approaches are not used in real time as the data is captured for analysis, prediction, and decision making. Embodiments described herein can increase the speed and simplicity of such decisions and enable higher throughput on existing equipment without requiring expert users to be involved with the analysis or operation of the equipment.

**[0022]** As used herein, the singular forms “a”, “an”, and “the” include singular and plural referents unless the content clearly dictates otherwise. For example, “predicting a peak” means “predicting one or more peaks”. Furthermore, the word “may” is used throughout this application in a permissive sense (i.e., having the potential to, being able to), not in a mandatory sense (i.e., must). The term “include,” and derivations thereof, mean “including, but not limited to.” The term “coupled” means directly or indirectly connected and, unless stated otherwise, can include a wireless connection.

**[0023]** As will be appreciated, elements shown in the various embodiments herein can be added, exchanged, and/or eliminated so as to provide a number of additional embodiments. In addition, as will be appreciated, the proportion and the relative scale of the elements provided in the figures are intended to illustrate certain embodiments of the present invention and should not be taken in a limiting sense.

**[0024]** The figures herein follow a numbering convention in which the first digit or digits correspond to the drawing figure number and the remaining digits identify an element or

component in the drawing. Similar elements or components between different figures may be identified by the use of similar digits. For example, 538 may reference element “38” in Figure 5, and a similar element may be referenced as 738 in Figure 7. Analogous elements between different figures may be referenced with a hyphen and extra numeral or letter. See, for example, elements 208-1 and 208-2 in Figures 2A and 2B, respectively. Such analogous elements may be generally referenced without the hyphen and extra numeral or letter. For example, elements 208-1 and 208-2 collectively may be referenced as 208. As will be appreciated, elements shown in the various embodiments herein can be added, exchanged, and/or eliminated so as to provide a number of additional embodiments. In addition, as will be appreciated, the proportion and the relative scale of the elements provided in the figures are intended to illustrate certain embodiments of the present invention and should not be taken in a limiting sense.

**[0025]** Figure 2A is a graph of a posterior predicted rate of change of chemical kinetics over time after measurement at two data points for a first example experiment. The horizontal axis indicates time 204 (in seconds) during which the chemical kinetics are being measured. The vertical axis indicates the rate of change 202 per second (1/s) of the chemical kinetics being measured. In this example experiment, the chemical kinetics relate to isothermal crystallization, which can be used to study solidification of semicrystalline polymers. The unfilled dots 212 represent data that has not yet been observed, which may be referred to as all data. The filled dots 214 represent observed or measured data. In Figure 2A there are two filled dots 214 starting on the left side of the horizontal axis at the relatively shorter time 204 (e.g., approximately 0.01 seconds in this example). The posterior predicted rate of change 216 is illustrated as a plurality of predictions where the line darkness is weighted by the probability (more probable predictions are darker). There are so many posterior predictions 216 that they cannot be seen individually. The darker shading represents a greater concentration of predicted rates of change 216, the lighter shading represents a lesser concentration of predicted rates of change 216. There are a few very faint individual predicted rates of change 216 that are visible rising above the darker and lighter shaded areas. In the examples of Figures 2A-2B, data is collected at 99.0 degrees Celsius.

**[0026]** The additional plot on top labeled “density” illustrates kernel density estimations of priors 218 (solid line) and posteriors 220 (dashed line). The top density plot represents the probability of the horizontal location of the predicted peak 206-1. The additional plot on the

right, labeled “density” illustrates kernel density estimations of priors 218 (solid line) and posteriors 220 (dashed line). The right density plot represents the probability of the vertical height of the predicted peak 206-1. The priors 218 represent a prior probability and the posteriors 220 represent a posterior probability as described in more detail below.

**[0027]** Bayesian modeling can be used to predict a peak 206 before all of the data 212 has been collected. If the confidence in the peak 206 is acceptable (within a threshold value), the program terminates data collection and then uses the probable peak 206 to make a decision regarding the state of the process. More specifically, the position 208-1 and/or height 210-1 of the peak 206 can be predicted using Bayesian modeling.

**[0028]** Bayesian modeling is a method of statistical inference in which Bayes’ theorem is used to update the probability for a hypothesis as more data becomes available. Bayesian modeling may be useful in the dynamic analyses of a sequence of data, such as measurement of a rate of change associated with chemical kinetics over time. Bayesian modeling derives a posterior probability 220 as a consequence of two antecedents: a prior probability 218 and a likelihood function derived from a statistical model for the observed data. The posterior probability 220 can be computed according to Bayes’ theorem:

$$P(H | E) = \frac{P(E | H) \cdot P(H)}{P(E)}$$

where H stands for any hypothesis whose probability may be affected by data. P(H) is the prior probability 218, which is the estimate of the probability of the hypothesis H before data E 214 is observed. Observed data E 214 is the data that is observed and used to compute the probability. P(H | E) is the posterior probability 220, which is the probability of any hypothesis H being correct given observed data E 214. P(E | H) is the probability of observing data E given prior hypothesis H, which is referred to as the likelihood. P(E) is the marginal likelihood, which is a likelihood function representing the probability of generating observed data from a prior.

**[0029]** In some embodiments, for the case of isothermal crystallization used to study solidification in semicrystalline polymers, the chemical kinetics can be modeled via the Avrami equation:

$$\alpha(t) = 1 - \exp(-Kt^{n_a})$$

$$\frac{d\alpha}{dt} = Kt^{n_a-1} \exp(-Kt^{n_a})$$

Once the predicted values of the empirical parameters  $K$  and  $n_a$  are known, the peak of this model can be predicted:

$$t_{max} = \left( \frac{n_a - 1}{K n_a} \right)^{1/n_a}$$

$$\left( \frac{d\alpha}{dt} \right)_{max} = K n_a t_{max}^{(n_a-1)} \exp(-K t_{max}^{n_a})$$

Other equations are possible. For example, reaction and/or crystallization kinetics can be modeled via the Sestak-Berggren equation:

$$\frac{d\alpha}{dt} = c(1 - \alpha)^n \alpha^m A_o \exp\left(-\frac{E_a}{RT}\right)$$

where  $\alpha$  is the extent of conversion (molten to crystalline, unreacted to reacted, etc.),  $t$  is time elapsed since the start of the reaction or crystallization process,  $K$  is the Avrami rate constant,  $n_a$ ,  $n$ ,  $c$ , and  $m$  are fitting parameters related to the crystallization or reaction order,  $A_o$  is the reaction rate at infinite temperature and the start of the reaction,  $E_a$  is the reaction activation energy,  $R$  is the ideal gas constant, and  $T$  is the system temperature. Prediction of values of empirical parameters of an equation describing the chemical kinetics can include the use of these parameters in the prediction of a peak, depending on the decision to be made. Although some examples herein include prediction of peaks, embodiments are not so limited. Furthermore, embodiments are not limited to the specific examples of chemical kinetic equations included herein. One of ordinary skill in the art can apply the embodiments disclosed herein to other equations describing the chemical kinetics. Table 1 includes example values and meanings for these parameters.

**Table 1**

| Empirical Value | Relates to                                                                               | Typical Values for Priors                                      | Justification for Priors                               |
|-----------------|------------------------------------------------------------------------------------------|----------------------------------------------------------------|--------------------------------------------------------|
| $K$             | Crystallization rate, or the time required to crystallize a certain fraction of material | 1 millisecond – 10 hours, normally distributed on a log scale. | Constrains the peak to the measurement range.          |
| $n_a$           | Crystallization order/regime, particularly at long times                                 | 1 – 4, uniformly distributed.                                  | This exponent is poorly defined outside of this range. |

|       |                                                                                      |                                        |                                                        |
|-------|--------------------------------------------------------------------------------------|----------------------------------------|--------------------------------------------------------|
| $n$   | Reaction order at long times                                                         | 0 – 4, uniformly distributed.          | This exponent is poorly defined outside of this range. |
| $m$   | Reaction regime, influencing primarily short times                                   | 0 – 4, uniformly distributed.          | This exponent is poorly defined outside of this range. |
| $E_a$ | Inverse probability of a reaction occurring relative to the thermal energy available | 0 – 400 kJ/mol, uniformly distributed. | These are typical ranges for many common reactions.    |

**[0030]** The existing data can be modeled to an equation using Bayes' Theorem. The model provides a statistical probability that, for example, the Avrami rate and Avrami index are any given value, which in turn gives the instrument and/or operator measurable confidence in the general location of the peak 206 (e.g., magnitude of the peak 206 and time at which it occurs) and whether the current measurement can be halted and continued at the next temperature. The operator and/or program can take the most probable location of the peak 206 and predict the position of the peak at the next experimental temperature. The probable location of the peak can be used to make a decision based on prior knowledge about the expected position of the peak given the particulars of the chemistry/physics being monitored. The entire automated modeling then repeats itself, giving readings every several seconds with a computational cost well within the specifications of a laptop computer as of 2023.

**[0031]** Using Bayesian modeling (inference), the probability  $P(H | E)$  for any given model to the data can be calculated. The distribution of all weighted probabilities can be used to calculate a posterior histogram 220, for example, to predict the position of the peak 206-1. The Bayesian model can be used to model data as it is collected in real time as each additional data point is collected. The model may use earlier measurements to optimize the priors  $P(H)$  and calculate the posterior prediction via a considered likelihood given the current data and adjusted priors accordingly. The model does not require user input during any part of the analysis. After collecting only two data points 214, the confidence in the peak location 208-1 and peak height 210-1 is very low as represented by the broad range of the posterior plots 220 illustrated by the dashed lines in the density plots. This indicates that more data points 214 need to be observed.

[0032] In each iteration, Bayesian modeling can make many predictions ( $H | E$ ) and calculate the probability of each prediction being correct with respect to possible predictions  $P(H | E)$ . The predictions are not random, but are based on priors. Each prediction includes a respective prediction for the empirical parameters (e.g.,  $K$ ,  $n_a$ ,  $n$ ,  $m$ , and  $E_a$ ). The predictions can be weighted by the probability. Each parameter can be plotted against its probability to provide a histogram centered on the predictions that are in the realm of the correct result. Neither an exactly correct prediction nor more correct predictions than incorrect predictions are necessary because predictions that are relatively more correct are weighted more heavily than predictions that are relatively less correct. A kernel density estimation can change a bar graph-type histogram into a smooth curve, such as is illustrated in Figures 2A-2B in the top and right graphs (labeled “density”). Statistical methods (e.g., mean, median, standard deviation, etc.) can be applied to the histogram to determine the most likely value for a respective parameter.

[0033] Figure 2B is a graph of a posterior predicted rate of change of chemical kinetics over time after measurement at six data points for the first example experiment. In Figure 2B there are six filled dots 214 starting on the left side of the horizontal axis at the relatively lesser time 204. The range on the vertical axis has increased from 0-9 in Figure 2A to 0-10 in Figure 2B. As compared to Figure 2A, the concentration of posterior predicted rate of change 216 is much narrower with essentially zero individual stray posterior predictions being visible. The predicted peak 206-2 is much easier to identify due to the greater concentration of posterior predictions 216. As compared to Figure 2A, the width of the posteriors 220 has decreased significantly, indicating an increased confidence in the prediction. After collecting only six data points 214, the confidence in the peak location 208-2 and peak height 210-2 is surprisingly high (given that the maximum had yet to be measured), as represented by the narrow range of the posterior plots 220 illustrated by the dashed lines in the density plots. This confidence is now within the user-defined preset threshold value and indicates that no more datapoints 214 need to be observed and the measurement may terminate early.

[0034] Although Figures 2A-2B are modeled via the equations described above, any relevant equation could be used. Embodiments provide the probability of any individual or collective empirical parameter being correct over prior guesses. Complex crystallization, degradation, and oxidation induction time equations (or summations thereof) are within the scope of the present disclosure.

[0035] Figure 3 is a graph of the percent standard deviation 323 in the prediction of the rate of change of chemical kinetics versus the number of data points collected 321 for an example experiment. Figures 2A-2B and Figure 3 correspond to the same experiment related to measurement of the crystallization of a material. The percent standard deviation 323 was calculated by taking 1000 posterior predictions and then calculating the relative standard deviation from the resulting histogram. The resulting modeling to the Avrami rate and Avrami index were acquired in a tenth of the time (10x less time) than by collecting all of the data and then analyzing it post-experiment. As illustrated in Figure 3, after approximately 40 data points, additional data leads to no better prediction. This result is unexpected and advantaged over traditional fitting methods because the collection of additional data points would not necessarily result in a static mean-squared-error or mean-squared-deviation since the additional data points would contribute to the average squared difference between the estimated values and the actual value (e.g., the percent standard deviation would continue to drop as more unnecessary data is collected), and in the case of repeat measurements it is understood that the signal-to-noise will improve by a factor of the square root of measurements. According to some previous approaches, it is unclear when the “fit” is good enough. However, according to at least one embodiment, the measurement can be halted and started again at the next parameter value (e.g., the next crystallization temperature). Additionally, according to the present disclosure, data analysis can be performed without concomitant human input at least partially because the priors allow for a broad range of guesses that quickly narrow down to a correct estimate of the most-likely solution. Traditional fitting methods may require much narrower initial guesses in order to successfully fit a limited amount of data.

[0036] Figure 4A is a graph of a posterior predicted rate of change of chemical kinetics over time after measurement at two data points for a second example experiment. The horizontal axis indicates time 404 (in minutes) during which the chemical kinetics are being measured. The examples described with respect to Figures 2A-2B involved relatively short time scales. The range of the horizontal axis in Figures 2A-2B is from 0 – 1.0 seconds. The range on the horizontal axis in Figures 4A-4B is from 0 – 90 minutes. The vertical axis indicates the rate of change 402 per minute (1/min.) of the chemical kinetics being measured. The unfilled dots 412 represent predicted data that has not yet been observed, which may be referred to as all data. The filled dots 414 represent observed or measured data. In Figure 4A there are two filled dots 414

starting on the left side of the horizontal axis at the relatively shorter time 404 (e.g., less than one minute in this example). The posterior predicted rate of change 416 is illustrated as a plurality of predictions where the line darkness is weighted by the probability (more probable predictions are darker). There are so many posterior predictions 416 that they cannot be seen individually. The darker shading represents a greater concentration of predicted rates of change 416, the lighter shading represents a lesser concentration of predicted rates of change 416. There are a few very faint individual predicted rates of change 416 that are visible rising above the darker and lighter shaded areas. In the examples of Figures 4A-4B, data is collected at 95.0 degrees Celsius.

[0037] The additional plot on top labeled “density” illustrates kernel density estimations of priors 418 (solid line) and posteriors 420 (dashed line). The top density plot represents the probability of the horizontal location of the predicted peak 406-1. The additional plot on the right, labeled “density” illustrates kernel density estimations of priors 418 (solid line) and posteriors 420 (dashed line). The right density plot represents the probability of the vertical height of the predicted peak 406-1. The priors 418 represent a prior probability and the posteriors 420 represent a posterior probability. After collecting only two data points 414, the confidence in the peak location 408-1 and peak height 410-1 is very low as represented by the broad range of the posterior plots 420 illustrated by the dashed lines in the density plots. This indicates that more data points 414 need to be observed.

[0038] Figure 4B is a graph of a posterior predicted rate of change of chemical kinetics over time after measurement at twenty-three data points for the second example experiment. In Figure 4B there are 23 filled dots 414 starting on the left side of the horizontal axis at the relatively lesser time 404 (e.g., approximately ten minutes in this example). The range on the vertical axis has decreased (zoomed in) from  $0 - 1$  in Figure 4A to  $0 - <1$  (less than one) in Figure 4B. As compared to Figure 4A, the concentration of posterior predicted rate of change 416 is much narrower with essentially zero individual stray posterior predictions being visible. The predicted peak 406-2 is much easier to identify due to the greater concentration of posterior predictions 416. As compared to Figure 4A, the width of the posteriors 420 has decreased significantly, indicating an increased confidence in the prediction. After collecting only 23 data points 414 over ten minutes, the confidence in the peak location 408-2 and peak height 410-2 is surprisingly high (given that the maximum had yet to be measured), as represented by the narrow range of the posterior plots 420 illustrated by the dashed lines in the density plots. This

confidence is now within the user-defined preset threshold value and indicates that no more datapoints 414 need to be observed and the measurement may terminate early. If the measurements ran the entire 90 minutes (as would be the case according to previous approaches), as much as 80 minutes of time would be wasted for each temperature at which the crystallization is studied. This method can be applied to a myriad of extended calorimetric or thermoanalytical techniques.

**[0039]** Figure 5 is a block diagram of a system for Bayesian modeling to predict chemical kinetics. The system can include a sensor 532 configured to measure chemical kinetics of a chemical 530. The chemical kinetics can correspond to a chemical reaction or to a phase change of a chemical 530. Examples of the sensor 532 include a calorimeter, such as a differential scanning calorimeter, a concentration sensitive detector, a molecular weight sensitive detector, a composition sensitive detector, or combinations thereof. Examples of concentration sensitive detectors include UV absorption, differential refractometer or refractive index detectors, infrared absorption, and density detectors. Examples of molecular weight sensitive detectors include low angle light scattering detectors and multiangle light scattering detectors. The chemical kinetics can correspond to crystallization, melting, chemical stability, chemical degradation, oxidation induction, curing, sorption, and/or desorption, for example. The sensor 532 can be configured to generate time series data 534 from sensing the chemical kinetics over a period of time.

**[0040]** The system can include a controller 536 coupled to the sensor 532 and to other equipment that can control the chemical 530. The other equipment can be a control system for temperature, introduction of chemicals, and the like. The controller 536 can include a processor 538 and memory resources 540 storing instructions executable by the processor 538 to cause the controller 536 to perform the functions described herein. An example of the controller 536 is described in more detail with respect to Figure 7. The controller 536 can be configured to initiate measurement by the sensor 532 of chemical kinetics of the chemical 530 over a period of time. The controller 536 can receive signals indicative of the data 534 representing the chemical kinetics associated with the chemical 530 from the sensor 532.

**[0041]** The controller 536 can be configured to recursively model the data 534 to an expected rate of change of chemical kinetics 544 using Bayesian modeling 542 before completion of the measurement over an entirety of the period of time. In some embodiments, the

expected rate of change can be based on the collected data 534 and other data collected before the measurement for an analogous experiment. In some embodiments, the expected rate of change can be based on the collected data 534 and empirical modeling of the rate of change 544 (e.g., based on the Avrami equation). The controller 536 can be configured to model data 534 to the expected rate of change 544 after the measurement at each discrete time at which the measurement has been conducted.

**[0042]** The controller 536 can be configured to recursively predict values of empirical parameters of an equation describing the chemical kinetics and/or a peak 506 in the rate of change 544 and calculate a probability 546 of the values of empirical parameters of an equation describing the chemical kinetics and/or peak according to the data before completion of the measurement over the entirety of the period of time. The controller 536 can be configured to cause the sensor 532 to stop 550 the measurement before completion thereof over the entirety of the period of time in response to the probability 546 being greater than a threshold value 548.

**[0043]** The controller 536 can be configured to output an indication of one or more of the predicted values of empirical parameters of an equation describing the chemical kinetics, the predicted peak 506, and the predicted rate of change of the chemical kinetics over the period of time. Although not specifically illustrated, the indication can be output to a display and displayed to a user. In some embodiments, the output can be provided to the other equipment in order to facilitate the taking of further actions based on the predicted values of empirical parameters of an equation describing the chemical kinetics and/or the predicted peak 506. The controller 536 can be configured to initiate the original measurement at a first temperature and to initiate a new measurement over the period of time at a second temperature by adjusting 552 a temperature (“ $\Delta T$ ”) for the chemical 530 in response to the probability 546 of the predicted values of empirical parameters of an equation describing the chemical kinetics and/or the predicted peak 506 being greater than the threshold value 548. The output can be provided to a plant control room and the measurement/modeling can be repeated. The measurement can be stopped early, and a new sample or parameter can be measured.

**[0044]** Figure 6 is a block diagram illustrating an example of a method for Bayesian modeling to predict chemical kinetics. The method may be performed, in some examples, using a computing system such as those described with respect to Figure 7. The method can be performed by processing logic that can include hardware (e.g., processing device, circuitry,

dedicated logic, programmable logic, microcode, hardware of a device, integrated circuit, etc.), software (e.g., instructions run or executed on a processing device), or a combination thereof. In some embodiments, the method is performed by or using the controller 536 shown in Figure 5. Although shown in a particular sequence or order, unless otherwise specified, the order of the processes can be modified. Thus, the illustrated embodiments should be understood only as examples, and the illustrated processes can be performed in a different order, and some processes can be performed in parallel. Additionally, one or more processes can be omitted in various embodiments. Thus, not all processes are required in every embodiment. Other process flows are possible.

[0045] As illustrated at 661, the method can include initiating a measurement of chemical kinetics over a period of time. The measurement can be initiated automatically or manually. Initiating the measurement can include initiating a series of measurements to be made at each of several discrete times within the period of time. The chemical kinetics can correspond to a chemical reaction or to a phase change of a chemical. The chemical kinetics can correspond to, for example, crystallization, melting, chemical stability, chemical degradation, oxidation induction, curing, sorption, or desorption. The measurement can be initiated at a first temperature.

[0046] At 663, the method can include recursively modeling data collected from the measurement to an expected rate of change of the chemical kinetics over the period of time using Bayesian modeling thereby yielding a predicted rate of change of the chemical kinetics over the period of time before completion of the measurement over an entirety of the period of time. In some embodiments, recursively modeling data means that after the measurement at each discrete time at which the measurement has been conducted, the observed data is modeled to the expected rate of change. This modeling is recursive because it repeats after each measurement or each subset of measurements.

[0047] At 665, the method can include recursively predicting values of empirical parameters of an equation describing the chemical kinetics based on the predicted rate of change of the chemical kinetics over the period of time and calculating a probability of the predicted values of empirical parameters according to the data before completion of the measurement over the entirety of the period of time. Recursively predicting the values of empirical parameters of an equation describing the chemical kinetics can include predicting one or more peaks in the rate

of change of the chemical kinetics. Each peak can correspond to a different time within the period of time. Recursively calculating the probability can include calculating a standard deviation of the plurality of peaks after probability density weighting thereof at each time at which the measurement has been conducted. Predicting the peak can include predicting a magnitude of the predicted peak at a time at which the peak is predicted to occur.

**[0048]** At 667, the method can include stopping the measurement before competition thereof over the entirety of the period of time in response to the probability being greater than a threshold value. The measurement can be stopped manually or automatically. Stopping the measurement can mean that the chemical kinetics at only a portion of the period of time.

**[0049]** Although not specifically illustrated in Figure 6, the method can include initiating a new measurement of chemical kinetics associated with a new experiment over the period of time without completing the measurement of the chemical kinetics associated with a previous experiment over the entirety of the period of time. As such, the method can advantageously expedite operations in a chemical process by increasing the efficiency of measurements and decreasing the time required to complete them. The method can include initiating a new measurement at a second temperature in response to the probability being greater than the threshold value.

**[0050]** Although not specifically illustrated in Figure 6, the method can include outputting an indication of predicted values of empirical parameters. Although not specifically illustrated in Figure 6, the method can include outputting an indication of the predicted peak. The indication of the predicted peak can be a graphical representation, an indication of a value of the height of the peak, and/or an indication of the location of the peak, as described herein. The indication(s) can be provided to a human operator and/or to other hardware components of a system in order to facilitate taking further actions based on the peak. For example, the method can further include adjusting a temperature based on the predicted values of empirical parameters and/or predicted peak. The adjustment can be manual or automatic.

**[0051]** Figure 7 is a block diagram of a machine within which a set of instructions, for causing the machine to perform various methodologies discussed herein, can be executed. Although not required for one or more embodiments, the machine 770 can be connected (e.g., networked) to other machines in a LAN, an intranet, an extranet, and/or the Internet. The machine 770 can operate in the capacity of a server or a client machine in client-server network

environment, as a peer machine in a peer-to-peer (or distributed) network environment, or as a server or a client machine in a cloud computing infrastructure or environment.

**[0052]** The machine 770 can be a personal computer (PC), a tablet PC, a set-top box (STB), a Personal Digital Assistant (PDA), a cellular telephone, a web appliance, a server, a network router, a switch or bridge, or any machine capable of executing a set of instructions (sequential or otherwise) that specify actions to be taken by that machine. Further, while a single machine 770 is illustrated, the term “machine” shall also be taken to include any collection of machines that individually or jointly execute a set (or multiple sets) of instructions to perform any one or more of the methodologies discussed herein.

**[0053]** The example machine 770 includes a processing device 738, a main memory 740 (e.g., read-only memory (ROM), flash memory, dynamic random access memory (DRAM) such as synchronous DRAM (SDRAM) or Rambus DRAM (RDRAM), etc.), a static memory 774 (e.g., flash memory, static random access memory (SRAM), etc.), and a data storage system 776, which communicate with each other via a bus 782.

**[0054]** The processing device 738 represents one or more general-purpose processing devices such as a microprocessor, a central processing unit (CPU), or the like. More particularly, the processing device can be a complex instruction set computing (CISC) microprocessor, reduced instruction set computing (RISC) microprocessor, very long instruction word (VLIW) microprocessor, or a processor implementing other instruction sets, or processors implementing a combination of instruction sets. The processing device 738 can also be one or more special-purpose processing devices such as an application specific integrated circuit (ASIC), a field programmable gate array (FPGA), a digital signal processor (DSP), network processor, or the like. The processing device 738 is configured to execute instructions 780 for performing the operations and steps discussed herein. The machine 770 can further include a network interface device 772 to communicate over the network 784.

**[0055]** The data storage system 776 can include a machine-readable storage medium 778 (also known as a computer-readable medium) on which is stored one or more sets of instructions 780 or software embodying any one or more of the methodologies or functions described herein. The instructions 780 can also reside, completely or at least partially, within the main memory 740 and/or within the processing device 738 during execution thereof by the machine 770, the

main memory 740 and the processing device 738 also constituting machine-readable storage media.

**[0056]** In at least one embodiment, the instructions 780 include instructions to implement functionality described herein, such as that corresponding to the controller 536 of Figure 5.

While the machine-readable storage medium 778 is shown in an example embodiment to be a single medium, the term “machine-readable storage medium” should be taken to include a single medium or multiple media that store the one or more sets of instructions. The term “machine-readable storage medium” shall also be taken to include any medium that is capable of storing or encoding a set of instructions for execution by the machine and that cause the machine to perform any one or more of the methodologies of the present disclosure. The term “machine-readable storage medium” shall accordingly be taken to include, but not be limited to, solid-state memories, optical media, and magnetic media.

**[0057]** Although specific embodiments have been described above, these embodiments are not intended to limit the scope of the present disclosure, even where only a single embodiment is described with respect to a particular feature. Examples of features provided in the disclosure are intended to be illustrative rather than restrictive unless stated otherwise. The above description is intended to cover such alternatives, modifications, and equivalents as would be apparent to a person skilled in the art having the benefit of this disclosure.

**[0058]** The scope of the present disclosure includes any feature or combination of features disclosed herein (either explicitly or implicitly), or any generalization thereof, whether or not it mitigates any or all of the problems addressed herein. Various advantages of the present disclosure have been described herein, but embodiments may provide some, all, or none of such advantages, or may provide other advantages.

**[0059]** In the foregoing Detailed Description, some features are grouped together in a single embodiment for the purpose of streamlining the disclosure. This method of disclosure is not to be interpreted as reflecting an intention that the disclosed embodiments have to use more features than are expressly recited in each claim. Rather, as the following claims reflect, inventive subject matter lies in less than all features of a single disclosed embodiment. Thus, the following claims are hereby incorporated into the Detailed Description, with each claim standing on its own as a separate embodiment.

### Claims

What is claimed is:

1. A method, comprising:  
initiating measurement of chemical kinetics over a period of time;  
recursively modeling data collected from the measurement to an expected rate of change of the chemical kinetics over the period of time, via Bayesian modeling, thereby yielding a predicted rate of change of the chemical kinetics over the period of time before completion of the measurement over an entirety of the period of time;  
recursively predicting values of empirical parameters of an equation describing the chemical kinetics based on the predicted rate of change of the chemical kinetics over the period of time and calculating a probability of the predicted values of empirical parameters according to the data before completion of the measurement over the entirety of the period of time; and  
stopping the measurement before completion thereof over the entirety of the period of time in response to the probability being greater than a threshold value.
2. The method of claim 1, wherein initiating the measurement comprises initiating a series of measurements; and  
wherein stopping the measurement before completion thereof comprises measuring the chemical kinetics at only a portion of the period of time.
3. The method of claim 1, further comprising initiating a new measurement of chemical kinetics associated with a new experiment over the period of time without completing the measurement of the chemical kinetics associated with a previous experiment over the entirety of the period of time.
4. The method of claim 1, comprising recursively modeling data and recursively predicting values of empirical parameters after the measurement at each of a plurality of discrete times at which the measurement has been conducted.

5. The method of claim 1, further comprising outputting an indication of the predicted values of empirical parameters; and  
adjusting a temperature based on the predicted values of empirical parameters.
6. The method of claim 1, wherein the chemical kinetics correspond to a chemical reaction or to a phase change of a chemical;  
wherein initiating the measurement comprises initiating the measurement at a first temperature; and  
wherein the method further comprises initiating a new measurement at a second temperature in response to the probability being greater than the threshold value.
7. The method of claim 6, wherein the chemical kinetics correspond to crystallization, melting, chemical stability, chemical degradation, oxidation induction, curing, sorption, or desorption.
8. The method of claim 1, wherein recursively predicting values of empirical parameters comprises recursively predicting a peak in the predicted rate of change of the chemical kinetics over the period of time; and  
wherein calculating a probability of the predicted values of empirical parameters comprises calculating a probability of the peak according to the data before completion of the measurement over the entirety of the period of time.
9. The method of claim 8, wherein recursively predicting the peak comprises predicting a plurality of peaks each corresponding to a different time within the period of time; and  
wherein recursively calculating the probability comprises calculating a standard deviation of the plurality of peaks after probability density weighting thereof at each different time.
10. The method of claim 8, wherein recursively predicting the peak comprises recursively predicting a magnitude of the peak and a time at which the peak is predicted to occur.
11. A system, comprising:

a sensor configured to measure chemical kinetics; and  
a controller coupled to the sensor and configured to:  
    initiate a measurement over a period of time;  
    recursively model data collected from the measurement to an expected rate of change of the chemical kinetics over the period of time, via Bayesian modeling, thereby yielding a predicted rate of change of the chemical kinetics over the period of time before completion of the measurement over an entirety of the period of time;  
    recursively predict a peak in the predicted rate of change of the chemical kinetics over the period of time and calculate a probability of the peak according to the data before completion of the measurement over the entirety of the period of time; and  
    stop the measurement by the sensor before completion thereof over the entirety of the period of time in response to the probability being greater than a threshold value.

12. The system of claim 11, wherein the controller is further configured to output an indication of one or more of the predicted peak and the predicted rate of change of the chemical kinetics over the period of time.

13. The system of claim 11, wherein the controller is configured to:  
    initiate the measurement over the period of time at a first temperature; and  
    initiate a new measurement over the period of time at a second temperature in response to the probability being greater than the threshold value.

14. The system of claim 11, wherein the chemical kinetics correspond to a chemical reaction or to a phase change of a chemical.

15. The system of claim 11, wherein to recursively model data, the controller is configured to predict the peak after the measurement at each of a plurality of different times at which the measurement has been conducted; and  
    wherein the expected rate of change is based on the collected data and data collected before the measurement for an analogous experiment.

16. The system of claim 11, wherein to recursively model data, the controller is configured to predict the peak after the measurement at each of a plurality of different times at which the measurement has been conducted; and

wherein the expected rate of change is based on the collected data and empirical modeling of the rate of change.

17. A non-transitory machine-readable medium storing instructions executable by a processor to:

recursively model data collected from measurement of chemical kinetics over a period of time to an expected rate of change of the chemical kinetics over the period of time, via Bayesian modeling, thereby yielding a predicted rate of change of the chemical kinetics over the period of time before completion of the measurement over an entirety of the period of time;

recursively predict values of empirical parameters of an equation describing the chemical kinetics based on the predicted rate of change and calculate a probability of the predicted values according to the data before completion of the measurement over the entirety of the period of time; and

output an indication of the predicted values of empirical parameters before completion of the measurement over the entirety of the period of time in response to the probability being greater than a threshold value.

18. The medium of claim 17, further comprising instructions to take an action with respect to the chemical kinetics based on the predicted values of empirical parameters.

19. The medium of claim 17, wherein the instructions to recursively predict the values of empirical parameters comprise instructions to recursively predict a peak in the predicted rate of change of the chemical kinetics over the period of time; and

wherein the instructions to calculate the probability of the predicted values of empirical parameters comprise instructions to calculate a probability of the peak according to the data before completion of the measurement over the entirety of the period of time.

20. The medium of claim 17, further comprising instructions to initiate the measurement; and

stop the measurement before completion of the thereof over the entirety of the period of time in response to the probability being greater than the threshold value.