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HEATING APPARATUS FOR REACTION KINETICS INVESTIGATIONS

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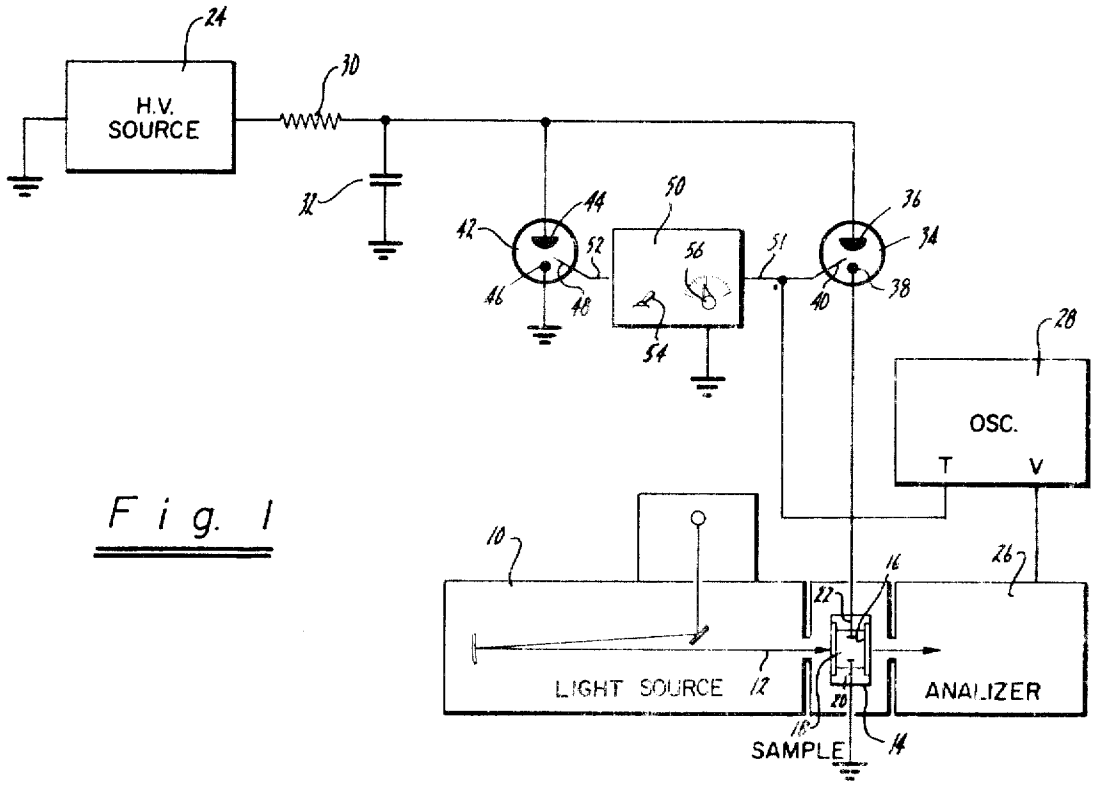


Fig. 1

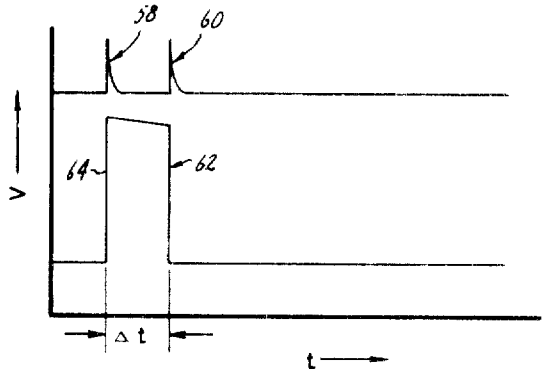


Fig. 2

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HEATING APPARATUS FOR REACTION KINETICS INVESTIGATIONS

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ABSTRACT OF THE DISCLOSURE

A high capacity voltage source is coupled across the sample cell electrodes by a spark gap tube triggered by a first pulse output from pulse generator. After an interval the voltage source is shorted out through a second spark gap tube triggered by a second pulse output from the generator. The current pulse passed through the sample during the interval causes a rapid increase in temperature by joule heating.

BACKGROUND OF THE INVENTION

This invention relates to systems for investigating the kinetics of chemical reactions of a sample of matter in which the thermodynamic equilibrium of the sample is perturbed by joule heating. Heretofore, it has been the practice to employ a capacitive discharge system in which the sample to be heated constitutes the essential resistive element of an RC discharge arrangement. In such an arrangement the maximum energy that is imparted to the chemical sample is $\frac{1}{2}CV^2$, where C is the capacitance and V is the voltage to which it is charged. This energy heats the solution in an exponentially decreasing amount and in a time which is determined by the time constant of the RC discharge, i.e. RC. The resistive element, i.e. the resistance of the sample, is a characteristic of the sample being studied and may vary considerably. Thus, the heating time for a given increment of temperature increase may be excessively long and obliterate the significance of measurements attempted on the associated perturbation of equilibrium. Accordingly, C has to be limited in order to keep the time constant, RC, short. In order to impart significant energy to the system for a fixed time constant, the remaining variable, the voltage, has often had to be increased to as high as 70 kv. Such high voltages are difficult to generate and handle and often cause breakover and uncontrolled discharges. There is, therefore, a need for a new and improved heating apparatus for reaction kinetics investigations.

SUMMARY OF THE INVENTION

In general, it is an object of the present invention to provide a new and improved heating apparatus for use in the investigation of the kinetics of chemical reactions which will overcome the above mentioned limitations and disadvantages.

Another object of the invention is to provide a heating apparatus of the above character in which the duration of the time in which heat is applied to the sample is adjustable so that it can be made less than the relaxation time of the reaction to be investigated.

Another object of the invention is to provide a heating apparatus of the above character in which a substantially constant heating current is applied to the sample over a given length of time, and further in which lower voltages are required for a given increment of temperature rise.

Another object of the invention is to provide a heating apparatus of the above character utilizing modified capacitor discharge techniques which are also useful in

obtaining useful temperature rises with high resistance samples.

Another object of the invention is to provide a heating apparatus of the above character in which trigger signals are provided for triggering associated display in instrumentations such as an oscilloscope.

In accordance with the above objects, there may be provided a photometer system for investigating the properties of a sample of material by light transmission and absorption techniques. The sample has a characteristic resistivity which permits a temperature change to be introduced into the sample by joule heating the same with a current pulse. A sample cell is provided for holding the sample of material and includes a pair of spaced electrodes in contact with the sample of material. One of the electrodes is connected to a common potential and the other is connected to a high capacity electrical energy generating and storage means. A first switch selectively connects the output of the source to the other electrode of the sample cell while a second switch selectively connects the output of the source to the common potential. Control means causes the first switch to become conductive at a predetermined time to cause the high voltage source to be connected to the other electrode so that current flows through the sample. Subsequently, the control means causes the second switch to become conductive after the elapse of a predetermined time interval to short out or crowbar the output of the source to the common potential. The interval between the first and second time is adjustable to a value small compared with the time required for the sample to reach a new chemical equilibrium caused by the step increase in temperature resulting from joule heating of the sample by the current pulse.

The above objects and features of the invention will become apparent from the following description and drawings.

DETAILED DESCRIPTION OF THE INVENTION

Referring to the drawings:

FIG. 1 is a diagram partly in schematic and partly diagrammatic of apparatus incorporating the present invention.

FIG. 2 is a graph depicting certain voltage waveforms appearing in the apparatus of FIG. 1.

Referring to FIG. 1, the heating apparatus of the invention is shown incorporated in a photometric system which is one form of apparatus in which it can be used. The system comprises a suitabe source **10** of light having an output beam **12** aligned with the input of a sample cell mount **14** supporting a cell **16** for containing the sample **18** of material to be tested. The cell **16** includes a pair of spaced electrodes **20**, **22** on each side thereof and in contact with the sample **18**. Electrode **20** is connected to a reference potential and electrode **22** is connected through circuitry to be described to a source **24** of high voltage.

Light passing through the sample and cell impinges upon an analyzer **26** which contains suitable circuitry such as a photomultiplier stage for determining the amount of light which has passed through the sample, and supplying an electrical signal indicative thereof to display means such as an oscilloscope **28**. When an electric current pulse is passed through the sample, as hereinafter described, its temperature is raised by a predetermined amount (usually about 10° C.). As is known, such a temperature jump or shift causes the constituents of the sample to assume a new chemical equilibrium which often effects the absorption properties of the sample. This effect may be an increase or decrease in the absorption of light beam **12** which increase or decrease is sensed by analyzer **26**, in a known manner.

The output of the high voltage source **24** is connected through a current limiting or charging resistor **30** to a charging capacitor **32** for storing a large quantity of energy at the voltage of source **24**. Capacitor **32** is characterized by having a large capacitance value so that its capacity as an electrical storage element will not be appreciably taxed during the time it is connected across sample, as hereinafter described.

Means forming a first switch is connected between the capacitor to the other electrode of the sample cell and consists of a gas filled spark gap tube **34** having spark gap electrodes **36**, **38** and a trigger probe or control electrode **40** for initiating breakdown of the gas so that the tube becomes conductive.

Means forming a second switch is connected between capacitor **32** and the common potential and consists of a second gas filled spark gap tube **42** also having spark gap electrodes **44**, **46** and a trigger probe or control electrode **48** for initiating breakdown. Each of the tubes **34**, **42** is of a conventional type such as a spark gap tube such as model GP–20A, made by EG&G Corporation of Bedford, Mass.

Control means is provided for causing the first switch to become conductive at a first time and for causing a second switch to become conductive after the elapse predetermined time interval from said first time. The control means comprises a pulse generator **50** which can include a monostable multivibrator, and having separate start and stop pulse outputs **51**, **52**. Start pulse output **51** is connected to the control electrode **40** of the first switch tube **34** and stop pulse output **52** is connected to the control electrode **48** of the second switch tube **42**. Pulse generator **50** may be any type providing a first pulse which can be initiated by suitable switch means **54** and which provides a second pulse delayed from said first pulse by a time which is variable, as by adjusting a dial **56** provided on the device. An example of such a pulse generator is that made by Hewlett-Packard and sold under the model designation 214A. Oscillscope **28** is also triggered by the start pulse appearing on control electrode **40**.

The following values have been found satisfactory for use in spectrophotometric investigations of the reaction kinetics of many chemical samples. High voltage source output **24**, 10 kv., capacitor **32**, 1μf. It will be appreciated that the capacitor **32** may be given an arbitrarily large value consistent with economics and necessary to supply the desired voltage for the required time.

The operation of the apparatus of the invention will now be described with particular reference to FIG. 2 wherein there is shown the timing relation between a start pulse **58**, a stop pulse **60**, and a current pulse **62**. The sample is disposed in cell **16** and the apparatus is connected as shown in FIG. 1 so that high voltage source **24** charges up capacitor **32**. Oscilloscope **28** is set to sweep at a rate fast enough to see the anticipated effect of heating the sample. Switch means **54** is then actuated so that a start pulse **58** is generated to trigger spark gap tube **34** into conduction and to start the sweep of the oscilloscope. Conduction of tube **34** causes a high voltage step **64** to appear across the sample as capacitor **32** discharges through the sample. After a selected time interval, Δt, has passed, pulse generator **50** provides a stop pulse **60** to trigger spark gap **42** which places a short across capacitor **32** so that the voltage pulse **62** is cut off. During the time interval Δt, which is much less than the RC time constant, the apparatus delivers an essentially square shaped current pulse through the sample which directly corresponds to the applied voltage pulse **62**.

By using the precisely controlled square current pulse of this invention, a capacitor charged to the same voltage (as in the exponential heating technique) provides more energy for heating in a given length of time and obtains the same degree of heating with lower initial capacitor voltages. If the resistivity of the solution being studied is high and the relaxation time (chemical) is long then the square current pulse described herein gives a usable temperature jump since the duration of the pulse, Δt, can be varied, whereas in exponential heating it would be inadequate.

It will be apparent that the improved heating apparatus described can be used in conjunction with other detecting systems such as conductometric, potentiometric and refractometric systems.

To those skilled in the art to which this invention relates, many changes and modifications will suggest themselves without departing from the invention. For example, while the use of spark gap tubes is shown herein, it is obvious that any device having a sufficiently high hold-off voltage and which can be suitably triggered into conduction can be substituted. Accordingly, it is to be understood that the disclosure and descriptions herein are illustrative of the invention and are not to be taken as a limitation thereon.

I claim:

1. In a system for investigating the kinetic properties of a sample material wherein the sample being investigated has a characteristic resistivity permitting a temperature change to be introduced into the sample by joule heating with a current pulse and including a sample cell in which the sample is placed having a pair of electrodes adapted to contact the sample with one of the electrodes being connected to a point of common potential; the improvement comprising a heating apparatus including:

a source of high voltage having one side thereof connected to the point of common potential;

a first switching means connected to the output of said high voltage source and in series with the other sample cell electrode;

a second switching means connected between said point of common potential and the output of said high voltage source in parallel with the circuit path defined by the series combination of the first switching means and the sample cell; and,

an adjustable pulse generating means connected to said first and second switching means for providing a first pulse to close said first switching means thereby connecting the high voltage source to the sample cell so that current flows through the sample and for providing a second pulse a predetermined time interval after said first pulse to close said second switching means thereby shorting the output of the high voltage source to the point of common potential and terminating the current flow through the sample, said time interval between said first and second pulses being adjustable to a value which is small compared to the time required for the sample to reach a new equilibrium caused by the step increase in temperature resulting from the joule heating of the sample by the current pulse.

2. A heating apparatus as defined in claim **1** wherein each of said switching means comprises a spark gap electrode discharge tube including a control electrode for initiating breakdown, the control electrode of each discharge tube being connected to said pulse generating means.

3. A heating apparatus as defined in claim **1** wherein said high voltage source includes a capacitor having a relative long time constant connected in parallel with said second switching means.

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Dedication

3,558,232.—*Victor J. MacCosham*, Menlo Park, Calif. HEATING APPARATUS FOR REACTION KINETICS INVESTIGATIONS. Patent dated Jan. 26, 1971. Dedication filed Aug. 23, 1971, by the assignee, *Beckman Instruments, Inc.*

Hereby dedicates to the Public the remaining term of said patent.

[*Official Gazette October 19, 1971.*]