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DIODES AS SENSORS IN SOLUTION THERMOCHEMISTRY

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Abstract

The advantages of using diodes as thermal sensors in solution thermochemistry are discussed and a simple, low-cost circuit for the use of diodes as temperature sensors is reported. In preliminary studies, the titration of TRIS and hydrochloric acid is used to compare the precision of thermistors and diodes in thermometric titrimetry. Several systems are assayed at various temperatures by enthalpimetric methods to illustrate the advantages of diodes as sensors for monitoring thermal methods capable of being used in quality control system.

Keywords: enthalpimetric methods, diodes as sensors, thermometric titrimetry

Introduction

As conventional solution thermochemistry developes there is a tendency to require more efficient sensing of the temperature changes within the analytical system. Developments are proceeding in at least two areas, one of microscale systems and another requiring precise and reproducible calibration of one or more sensors, either for individual measurements capable of precise comparisons, or for the simultaneous measurement of more than one system, coupled with simultaneous inter- and intra-comparison of results from present and previous systems. Examples are to be found in systems using on-line flow analysis

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by solution thermochemistry and in quality control systems where comparisons have to be made between different batches of analyte. The uses in differential measurement of analytical systems are in process of development.

Various types of sensors have been used for indicating temperature changes in the techniques of solution thermochemistry. The earliest were mercury-in-glass thermometers. These, generally Beckmann type thermometers, had the great disadvantage that the volume of mercury necessary to give the required sensitivity to the technique required large volumes (ca. 50–100 ml) of analyte solution and a very slow rate of addition of titrant, often batchwise addition, in order to realise thermal equilibrium in the system at all times. Although notable work was reported and has been reviewed in textbooks dealing with the techniques [1, 2] it is generally accepted that the slow development of the techniques of analytical solution thermochemistry resulted from the necessity to use this type of temperature sensor. Although the use of multiple junction thermocouples was first reported in 1941 by Muller [3] and later for some simple titrations [4] the size of a multijunction and the poor response prevented developments in this area.

It is generally accepted that the major advance in detectors used in thermometric titrimetry resulted from the introduction of the thermistor as the sensor [5]. Since then the thermistor, has been more or less exclusively used as the temperature sensor in solution thermochemistry. The thermistor is generally incorporated in one arm of a D. C. Wheatstone bridge, relating the 'off balance' of the bridge to the change in temperature of the analyte system. The thermistors used generally have a small sensor bead of semi-conducting material (ca. 0.5 mm diameter) coated with a glass film against chemical attack. The response time to temperature change is usually less than 1 second when the thermistor bead is immersed in a liquid. (Thermistors coated with a hydrofluoric acid resisting coating [6] have slightly longer response times.)

In a conventional Wheatstone bridge used in solution thermochemistry, the resistance of the variable resistance arm, use as a comparator for the thermistor, is adjusted so that at the constant initial temperature no potential difference exists between the terminals of the potentiometric recorder. As the temperature of the sensor alters, the resistance of the thermistor (which generally has a temperature coefficient of resistance of the order of 0.04 ohms per ohm per degree centigrade) alters and produces an 'off-balance' voltage across the bridge. This voltage can be related, directly or indirectly, to the change in the voltage applied to the recorder. During this time, current is flowing through the high resistance thermistor producing a small Joule heating effect. Whilst in reactions involving 15–30 ml of sample solution this Joule effect is usually insignificant, on a sample of less than 1 ml the heating effect is of significance and may be an appreciable part of the enthalpy change in the system.

The relationship between the resistance of a thermistor and temperature is :

$$R_1 = R_2 \exp B(1/t_1-1/t_2)$$

where R_1 and R_2 are the resistances at the specified temperatures t_1 and t_2 which are the two temperatures concerned with the temperature change in the system, B is a constant operating over all but the extremes of the temperature range of the thermistor. Thus the change in resistance with temperature is non-linear and the relative change in resistance for unit change in temperature depends upon the *initial* temperature of the system.

In a simple Wheatstone bridge system the sensitivity of the bridge, viz: the change in off-balance voltage occasioned by the change in resistance of one of the arms, is a maximum when all of the arms have the same resistance. It therefore follows that calibration curves relating enthalpy changes and recorded voltage changes, as used in enthalpimetry, are strictly comparable, for any particular system, only if they are obtained over the same small temperature range. Various workers have proposed alternative systems, including modified Wheatstone bridges, to obtain constant sensitivity. These and methods of producing reproducible changes from thermistors have been reviewed by Vaughan [7] and Carr [8].

However, for practical purposes, most workers have relied on fairly simple Wheatstone bridge systems and thermostatting of the reaction systems to give thermally reproducible conditions for calibration and subsequent assays involving enthalpimetry. This has been found to be inconvenient if non-ambient conditions are used and work has been done to produce a system which is capable of being calibrated at one temperature and then used at the various temperatures appropriate to the particular reaction conditions.

Some preliminary work involving the use of a diode has been reported earlier [9] and the present study extends that work.

Diodes are semiconductors which are heavily doped with either *p*- or *n*-type materials. The basic semiconductor is made from germanium or silicon, the latter giving diodes which are superior for application to temperature measurements because of lower current requirements. The output voltage of a diode can be made absolutely linear with little difficulty, irrespective of the temperature of use. The linearity of the output from a diode depends upon the reverse current being small relative to the forward current. In this respect silicon diodes are preferable to the corresponding germanium diodes.

A diode, like a thermistor, is a voltage sensor. Its response is almost independent of its internal current, (its sensitivity increases slightly as the current decreases). It should be operated at constant current in order to produce an absolutely linear voltage/temperature response. Diodes can be well matched for response to temperature change irrespective of the original temperature and the matching can be made precise by controlling the current through the diode. A diode system requires a more complicated bridge system than does a thermistor and since diodes are not commercially available as temperature sensors, some preliminary work on the encapsulation with a coating which is insensitive to chemical attack and has a rapid response to temperature change is reported.

Experimental

Selection of the diode

To select the diode from those commercially available, it was necessary to coat the diode for use in experimental conditions. It is then necessary to ascertain the voltage/temperature characteristics and incorporate the selected diode in an electronic bridge circuit capable of giving amplification of the signal to the range of voltages expected for the various envisaged uses of the complete system.

Coating the diodes

Throughout this part of the programme of study both thermometric and enthalpimetric titrations were done using TRIS as the titrand and hydrochloric acid as the titrant. The reaction vessel contained both the thermistor and the diode and the temperature changes were recorded on a twin pen recorder.

Several different techniques were used for coating the diode and its supporting leads.

Experience had shown that a thin glass coating on thermistors was generally useful, thus attempts were made to envelope the diode and its leads in glass. This proved to be impossible since the heat transferred to the diode by the molten glass caused the diode junction to fracture.

Other coating materials investigated included a commercially available polyurethane coating and a synthetic rubber solution, both of which could be applied at ambient temperatures, the former was 'cured' using a peroxide initiator; a silicone 'wax', which could be applied at approximately 100°C and polyethylene. Of these only the rubber coating and the polyethylene were able to withstand both the acidic and alkaline conditions used in the study. The rubber coating was not able to withstand some of the non-aqueous solvents used in some studies.

Using polyethylene, the coating is applied by gently melting polyethylene flakes, dipping in the diode and its supporting leads, removing the dipped diode from the melt and gently rotating the diode and leads until the polyethylene solidifies as a uniformly thin coating. Coating with the rubber was simpler, the diode and leads were dipped into the rubber solution, gently rotated to obtain a uniform thin layer and allowed to dry. The thermograms and enthalprograms obtained using such coated diodes were acceptable in shape and the curvature at the equivalence point was less than that using a thermistor in the system.

Diodes

To select the most appropriate diode as the temperature sensor, the forward voltage characteristic curves and the voltage/temperature characteristic curves were measured for a series of silicon and germanium coated and uncoated diodes and their sensitivities (dV/dT) were determined at particular constant currents. Typical results are given in Table 1.

Table 1 Sensitivities of various types of *pn*-junction diodes (uncoated) at a constant current of 10 microamps

Diode	Temperature range/ °C	Sensitivity/ $mV\cdot°C^{-1}$
Si Diodes		
0A20201 (+)	0-100	–2.68
1N4148 (+)	0-100	–2.47
1n4148 (*)	0-100	–2.80
BY206 (+)	0-100	–2.85
1N4007 (+)	0-100	–2.66
Ge Diodes		
0147 (*)	20-26	–1.16
0A90 (*)	20-26	–2.06
0A91 (*)	20-26	–2.22

(+) Diodes obtained from Farnell Electronic Ltd.

(*) Diodes obtained from Radiospares Ltd.

The voltage/temperature characteristics for the silicon diodes were linear over the temperature range of 0–120°C. Over a much shorter range (20–40°C) there was a pronounced concavity of the curves for the germanium diodes.

The decrease in the sensitivity caused by coating the silicon diodes was approximately 0.4% at 0°C and decreased linearly to zero at 100°C.

Effect of variation in the value of the forward constant current

Decreasing the value of the forward constant current for a particular diode increased to voltage/temperature characteristic. For example: Diode 1N4148.

With a forward current of 1 microamp: $dV/dT = -3.48$ mV/°C. With a forward current of 10 microamp: $dV/dT = -2.80$ mV/°C.

Although with low values of the forward constant current there was an increase in the sensitivity, there was also an increase in the electronic noise level with low currents and for practical purposes a constant forward current of 10 microamps was chosen.

Construction of the temperature probe

The probe consists essentially of *p-n* junction silicon diode. This is soldered to a copper wire insulated with pvc and is inserted into a glass tube (ca. 6 mm i.d.). The end of the tube is dipped into the selected coating material, (depending on the use for which the sensor is intended), covering the part of the diode and the tube walls. (Fig. 1) Connection to the constant current source is made via a suitable jack-plug.

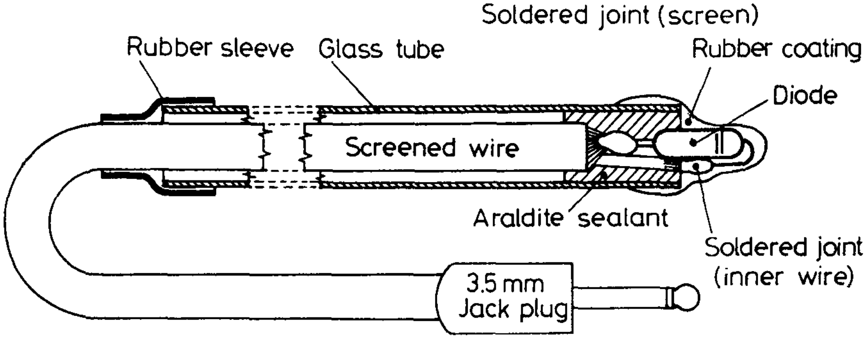

Fig. 1 Diode temperature probe

Diode bridge system

Details of the diode bridge system are shown schematically in Fig. 2. The diode bridge has 4 parts:-(i) constant current source, (ii) buffer circuit, (iii) filter circuit, (iv) amplifier circuit.

The constant current source

In this section of the bridge, the LM334Z semi-conductor integrated circuit is a three terminal programmable current source with precise current regulation and a dynamic voltage range of 1–30 volts. The resistance *R* was set at a predetermined value to give a current of 10 microamp. (This circuit, fitted with an ammeter, was used to obtain the voltage-temperature characteristics of the various diodes tested in the work.)

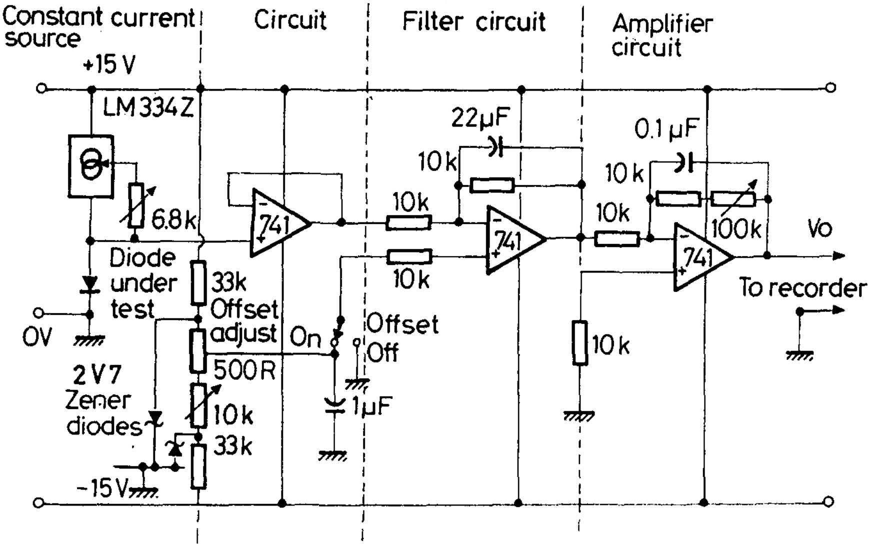

Fig. 2 Circuit used for the selection of semiconductor diode temperature sensors

Buffer circuit

A high input impedance with a unity gain amplifier is used as a buffer circuit to read the voltage drop occurring across the diode. This buffer circuit presents negligible shunting effects to the diode and gives an output that is a temperature related voltage from a low impedance source and is thus suitable for signal processing.

Filter circuit

The signal from the buffer circuit is smoothed by a first order low pass filter constructed from an operational amplifier with a resistance and capacitance network. The filter eliminates unwanted signals from stirring effects and mains-borne electrical noise.

Amplifier circuit

A simple operational amplifier is used to increase the signal to a size capable of being used by the potentiometric recorder to hand.

Thermometric bridge system

Details of the thermometric bridge incorporating an operational amplifier and associated power supply system have been previously described [10].

Titration apparatus

(i) Thermometric titrations

(a) Titrant delivery system

An 'EYELA' microtube pump (Tokyo Rikakikai Co.) was used. The rate of delivery was changeable by means of a speed controller on the pump. The actual delivery rate for each set of titrations was determined via the gravimetric determination of the amount of water delivered in a known time (usually 500 secs).

(ii) The reaction vessels

Each cell was constructed from a cylinder of polyethylene and had a nominal internal diameter of 2.5 cm (a cross section of approx. 5 sq.cm.) and height of 7 cm.

Polyethylene was chosen because of its resistance to chemical attack, its low thermal conductivity and heat capacity. Additional insulation was provided by encasing the vessels in a block of 'Styrafoam' to maintain adiabatic or quasi-adiabatic conditions. The cell was closed with a loose fitting polyethylene lid (approx. 1 cm thick) drilled to hold the titrant delivery tube and the temperature sensor. Each cell was stirred using a glass encased magnetic stirrer.

Comparison of thermistors and diodes for work at elevated temperatures

One of the main disadvantages of thermistors is the pronounced concavity of the resistance *vs.* temperature curves of all types of thermistors normally used in thermometric and enthalpimetric studies. At elevated temperatures, say at 80–100°C, the change in resistance with change in unit temperature is significantly less than that at normal ambient temperatures. This decreases the sharpness of the equivalence points in thermometric titrimetry and may have an effect on the precision of the measurement of the volume of titrant used. In enthalpimetry it means that using calibration curves prepared at temperatures different to those used for the assay, gives incorrect values. This necessitates thermostatting the reaction vessel and all solutions used in assays for quality control or for comparison purposes. Such thermostatting increases the complexity and cost of the equipment used.

The diodes used in this study have practically linear relationships between the change in signal and the change in temperature from 5–120°C. Thus, theoretically, the same amount of a chemical reaction will cause the same change in the signal at any temperature between 5–120°C. This removes the need for thermostatting the equipment and the reagent solutions.

Using the heated reaction vessel and block previously described [10] in which the temperature of an aluminium block is maintained to 0.01°C at any chosen temperature between 15 and 90°C samples of various materials were assayed at different temperatures using both thermistors and diodes to monitor the temperature changes. Calibration curves for each material were prepared at ambient temperatures.

Enthalpimetric determinations

To facilitate the comparison of the values obtained, the sensitivities of the electronic bridges were adjusted so that the recorder signal for each sample assayed at ambient temperature was 100 divisions.

Results: Table 2.

Table 2 Enhalpimetric methods

System Sample/Reagent	Recorder signal at t/°C Diode/Thermistor				
	Amb(16)	25	50	70	85
Barium/Sulphate	100/100	100/98	100/91	100/84	100/68
TRIS/HCl	100/100	100/97	100/83	100/74	100/69
Phosphate/Calcium	100/100	100/97	100/90	100/85	100/68

Thermometric titrations

Aliquots of several series of solutions of various analytes in different types of titrations viz.:-, aqueous systems; -acid/base; precipitation reactions;

Non-aqueous systems: -catalysed thermometric; complexation reactions were titrated at different temperatures.

Results see Table 3.

Discussion

From the results shown in Table 3 it may be seen that for thermometric titrimetry neither of the two systems of temperature sensing have any advantages over the other. However, Table 2 indicates that for use in enthalpimetry, diodes are obviously advantageous.

The thermodiode and amplifier combination selected for this work are capable of detecting temperature changes of the order of 0.001°C using the maximum amplication. The limiting factor is the concurrent amplification of extraneous circuit noise. Although compared to diodes, thermistors have some useful advantages there are some disadvantages, which must be considered when choosing a system for use in routine quality assurance and for work involving possible ambient temperature changes which would necessitate the in-

Table 3 Thermometric titrations

		Aqueous systems				
Titrant / Analyte			Temperatures/°C			
HCl / TRIS		20	40	60	80	
Ag^+ / Br^-		20	40	60	80	
		Non-aqueous systems				
(i) Perchloric acid in glacial acetic acid/sodium acetate in glacial acetic acid+acetic anhydride						
Temperatures/°C	20	30	40	50	60*	
(ii) 2, 2 dipyridyl in toluene/zinc diethyl in *n*-octane						
Temperatures/°C	20	30	40	50	60	70*

The precision of determination of the equivalence point was practically the same for any particular series. Either the thermistor or the diode was equally acceptable in use.

For the non-aqueous systems at the higher temperatures (*) loss of solvent caused by evaporation and stirring produced pronounced curvature and 'dragging' of the equivalence points and made the titrations not practical.

troduction of expensive and cumbersome thermostatting of the reaction cell and all reagent and sample reservoirs. Several aspects must be considered including:

(i) the minimum temperature change response available i.e. the maximum sensitivity of the sensor. (ii) the time of response, (iii) the range of temperature for which a particular system can be used, and (iv) the ease of replacing the sensor in routine work involving comparisons of values obtained from different experiments.

For example: With regard to the sensitivity, thermistors can provide a voltage/temperature effect which is often approximately four times greater than that from a typical silicon junction diode, and the reported limits of detectable temperature changes by thermistors has steadily improved from 0.005°C [11] to about 3–15°C [12–14]. However, for most work, other than microcalorimetry, such sensitivities are not required and any systems requiring such sensitivities will also require a much higher order of thermostatting, to prevent non-reaction temperature changes having significant effects. Commonly used enthalpimetric systems do not require such sensitivities.

With regard to response times, the response time of the diode is less than 1 sec which makes it useful for thermometric titrations [8].

Although silicon diode thermometers with response times of the order of 0.006 sec have been reported [15] these are both very expensive and generally beyond the needs of routine assay work. The response times of the low cost system described in the present work is less than 0.01 sec. The minimum response times of most commonly used thermistors is of the order of 0.5 secs. For fast on-line analysis of systems with a high through-put, this can be a limiting factor.

The use of diodes eliminates two of the main problems found in analytical solution thermochemistry which are the non-linear response of the thermistor sensor and the non-linear output of the Wheatsone bridge caused by the changes in the resistance of the thermistor sensor when used over the relatively modest temperature ranges common in aqueous solution titrimetry.

Attempts to eliminate the first problem using a large passive shunt [16] or a network of three or more thermistors have had limited success [17]. It has been reported [18] that the linearity of the output of a typical Wheatstone bridge was less than 1% for a temperature change of 1°C. In attempts to eliminate this non-linearity, several workers have applied numerical methods for the purpose of linearisation, but their use is tedious and requires electronic computer facilities. Examples of attempts to obtain linearity have been reviewed [8, 9] but most of the examples require the introduction of complex and costly equipment. The thermodiodes and the electronic bridge used in the present system ensure linearity over a range of temperature change greater than that found in aqueous titrimetry.

Another problem associated with thermistor sensors is the difficulty in matching the characteristic responses of two or more thermistors. In temperature measurement systems such as the enthalpimetric methods used in assay systems or for quality assurance, the ability to interchange sensors without requiring re-calibration of the instrument is very important.

Replacement of damaged sensors, simultaneous or sequential measurements at multiple and various locations in a system and uniform calibration of instrumentation all require that all temperature sensors of a given characteristic be interchangeable within the required accuracy of the measurements to be made. Statistical analysis of the results reported to obtain Table 1 shows that for any of the diodes used in the present work, the change in forward voltage is practically linear (coefficient of linearity 0.9995) with changes in temperature over the range 273–373 K at a constant forward current of 10 microamps. Results also indicated that the identical characteristics are obtained for any two of the diodes of the same type studied over the range of temperature.

The advantages of the linearity of the voltage/temperature relation of the diodes and the ease of matching diodes are clearly demonstrated and implies that the use of thermostatted reaction vessels and sample and reagent reservoirs is not necessary. This is of great importance in the design of systems for industrial on-line analysis. It means that except for economical reasons, such as energy conservation, the reaction vessel and conduit pipes leading to the assay system need not be lagged, making them more readily accessible for maintenance including replacement of sensors. The diode system lends itself to automation since all the electronic circuitry is simple and robust.

Screening of the diode and filtering of the signals is essential to prevent noise pick-up from alternating electrical fields from mains and from radio and T. V. circuits.

The presently proposed system is both sensitive, robust and of a cost low enough to allow for its use in on-line assay work. The sensitivity of the system is such that semi-micro and micro amounts of some analytes may be assayed.

The use of diodes and the associated bridge system as temperature sensors in enthalpimetry has great commercial potential in a wide field of applications. Such a system has already been used with commercially acceptable results in assay work in a cement factory for some months.

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Zusammenfassung — Es werden die Vorteile der Verwendung von Dioden als Thermosensoren in der Thermochemie von Lösungen diskutiert und ein einfacher, kostengünstiger Stromkreis für die Verwendung von Dioden als Temperaturfühler beschrieben. In vorangehenden Studien wurde die Titration von TRIS und Salzsäure zum Vergleich der Genauigkeit von Thermistoren und Dioden in der thermometrischen Titrimetrie verwendet. Einige Systeme wurden bei verschiedenen Temperaturen mittels enthalpimetrischen Methoden geprüft, um die Vorteile von Dioden als Sensoren für das Monitoring thermischer Methoden zu demonstrieren, die zur Anwendung in Qualitätsprüfungssystemen fähig sind.