

## Thermal behaviour of Landolt reactions studied by heat exchange calorimetry of batch type

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(Received 29 November 1991)

### Abstract

The Landolt reaction, known by the nickname of a “clock reaction”, is exemplified by redox reactions in aqueous solution, including that between potassium iodate and sodium hydrogen sulphite. In the presence of starch, the colourless solution becomes bluish violet at a certain time interval after mixing. The thermal behaviour of the clock reaction was studied for estimating the rate of heat evolution and the total heat effect by heat exchange calorimetry of batch type. To start the reaction, the weighed sample crystals of sodium hydrogen sulphite were added to the aqueous potassium iodate solution in the sample vessel in the calorimeter. The heat of solution of sodium hydrogen sulphite was observed separately in water. The experimental concentration ranges of potassium iodate and sodium hydrogen sulphite were selected according to the requirements of the calorimeter. The total reaction time was also estimated from curves of the rate of heat evolution. The total heat effect was obtained as the difference between the observed heat of reaction and the heat of solution, and depended only on the amount of sodium hydrogen sulphite. The heat of reaction was estimated to be  $-239.9 \pm 5.5$  kJ per mol of sodium hydrogen sulphite at  $25.0 \pm 0.1^\circ\text{C}$ .

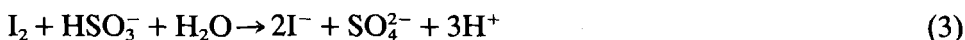
### INTRODUCTION

The Landolt reaction includes such redox reactions in aqueous solution as that between iodate and hydrogen sulphite ions. It is well known by the nickname of a “clock reaction”, and is often used for chemical demonstrations. Belousov also referred to the reaction in his report [1]. In the presence of starch, the liberated free iodine changes the colour of the

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solution to bluish violet at the moment when hydrogen sulphite has been consumed by the excess of iodate. The reaction may proceed in three steps



The reaction mechanism has already been elucidated. Reactions (1) and (2) are slow, and reaction (3) is fast. Katsuyama et al. [2] analysed the concentration changes of species such as  $\text{I}^-$ ,  $\text{I}_2$ ,  $\text{H}^+$ ,  $\text{IO}_3^-$ ,  $\text{HSO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{SO}_3$  and  $\text{HSO}_4^-$  by computer simulations, and discussed the rate constants estimated by Skrabal and Zahorka [3].

Heat exchange calorimetry [4] was developed to measure easily the rate of heat evolution  $q$  and the total heat effect  $Q$ . Sample and reference vessels were fixed differentially in a precision water bath. The heat evolved by a chemical reaction or electric heating in the sample vessel was exchanged freely with the ambient water, the temperature of which was controlled within a narrow range [5]. The heat transfer was expressed by a simple differential equation. In each vessel a thermistor was installed as a thermal sensor. The thermal phenomena in the sample were detected by the thermistor and converted into electric signals via a Wheatstone bridge. Analog computation was carried out to estimate  $q$  and  $Q$  from the observed signals. The thermal behaviour of Belousov–Zhabotinsky reactions has been studied by this type of calorimetry [6].

In the present report, thermal phenomena of the clock reaction initiated by dissolving sodium hydrogen sulphite crystals in potassium iodate solution were studied in the continuously stirred solution by heat exchange calorimetry. As for the reactions, it was not necessary to take the change of heat capacity into consideration. Therefore the calorimetry of batch type was selected in view of the simple assembly of the calorimeter and its ease of operation. The observed  $q$  and  $Q$  values were related to the mechanism of the Landolt reaction.

## EXPERIMENTAL

### *Reagents*

All the reagents used were of guaranteed grade from Wako Chemical Industrial Co., Osaka, and were used without further purification. Sample crystals of potassium iodate and sodium hydrogen sulphite were dried in an air bath before use. Deionized and distilled water was boiled just before use.

## Apparatus

The heat exchange calorimeter was assembled on almost the same lines as reported previously [4–6]. Two glass bottles of about 100 cm<sup>3</sup> were used as sample vessel S and reference vessel R, and were fixed differentially in the water bath. A glass box 23 × 30 × 27 cm<sup>3</sup> in size having all its surfaces covered with 5 cm thick styrofoam insulator boards was filled with 12 l of water, which was agitated by a motor-driven stirrer (35 W, PS-1, Yamato Kagaku Co., Tokyo). The temperature of the bath water was controlled by the reported method [5] to within  $\pm(2-3) \times 10^{-4}$  K at  $25.0 \pm 0.1^\circ\text{C}$ . In each vessel were installed a thermistor as thermal sensor, a sample inlet, a heater element for Joule heating and an iron bar for the magnetic stirrer. The thermistors in the sample and in the reference vessels were incorporated in two arms of a Wheatstone bridge, from which the out-of-balance voltage was fed to an analog computation circuit for calculation of  $q$  and  $Q$  after amplification. The output voltage was obtained from operational amplifiers (LF356, National Semiconductor Corp.). The calculated  $q$  and  $Q$  value were recorded simultaneously on a two-pen  $Y-t$  recorder (R-OX, Rika Denki Co., Tokyo). A metal-wound resistor (0.125 W, 100.5  $\Omega$ , Tama Denki, Co., Tokyo) coated with epoxy resin to prevent access of chemicals was used as the heater element. A Cahn gram electrobalance was used for weighing to within  $\approx 0.01$  mg.

## Procedure

The vessels S and R, each containing 50 g of the potassium iodate solution, were set in an aluminium frame with a magnetic stirrer of submerged type and fixed in the water bath. All the electrical devices in the calorimeter, such as electronic circuits, the temperature control system, the motor-driven stirrer and the recorder, were powered. Their warming-up time was almost the same as that for thermal equilibrium in the calorimeter. Time constants in the analogue circuit were adjusted to be equal to those of the calorimeter by using variable resistors in the circuit for the electrical heating process. Almost the same amount of heat effect as that from a single run of the chemical reactions was given to the sample solution from a stabilized power circuit (521C, Metronix Co., Tokyo). Before and after the chemical reaction run, Joule heats were measured. The weighed sample crystals of sodium hydrogen sulphite were dropped through the sample inlet of vessel S without removing the cover board, and the clock reaction was started. The heat of solution of sodium hydrogen sulphite was observed similarly after replacing the potassium iodate solution by water.

## RESULTS AND DISCUSSION

Appropriate concentrations of potassium iodate and sodium hydrogen sulphite were selected to maintain accuracy in operations with small sample size and in the calorimetric estimation, as well as affording a total reaction time long enough to prevent errors in measurement of time or length on the chart. As the dissolution of the potassium iodate crystals took a finite time, the sodium hydrogen sulphite crystals were directly added to the sample vessel from the outside of the calorimeter without removing the insulator board. The time necessary for the dissolution was therefore negligibly small compared with the total reaction time  $t$ . Errors from the temperature difference between the sample crystals at ambient temperature and the solution kept at 25.0°C may be smaller than other errors.

As is usual, Katsuyama et al. [2] adjusted the ionic strength by adding sodium perchlorate. In the present work, however, neither starch, for visual indication of the end point, nor sodium perchlorate was added in order to avoid their calorimetric effects.

Typical thermograms of  $q$  and  $Q$  recorded simultaneously on a strip chart recorder of two-pen type are shown in Fig. 1. The reaction was started by adding sodium hydrogen sulphite to the sample vessel. The start point is shown by an arrow in Fig. 1, and also in Figs. 2 and 3. The interval  $t$  was the time interval from the start point to the end point, which was indicated by the return of the  $q$  curve to the starting baseline. Each endothermic peak located just after the arrow in the traces of  $q$  and  $Q$  corresponded to the heat of solution produced by dissolving the sodium hydrogen sulphite crystals.

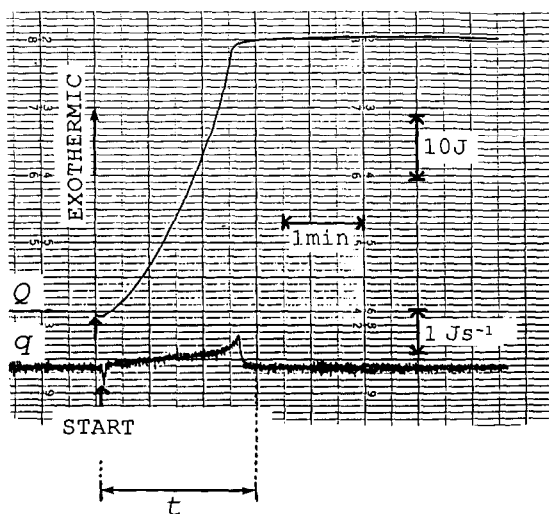


Fig. 1. Typical observed traces of  $q$  and  $Q$ .

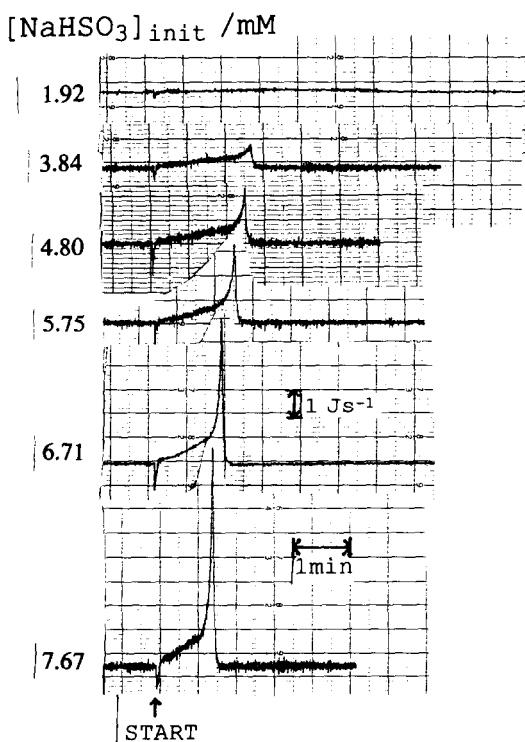


Fig. 2. Traces of  $q$  at several  $[\text{NaHSO}_3]_{\text{init}}$  observed in 5 mM  $[\text{KIO}_3]_{\text{init}}$ .

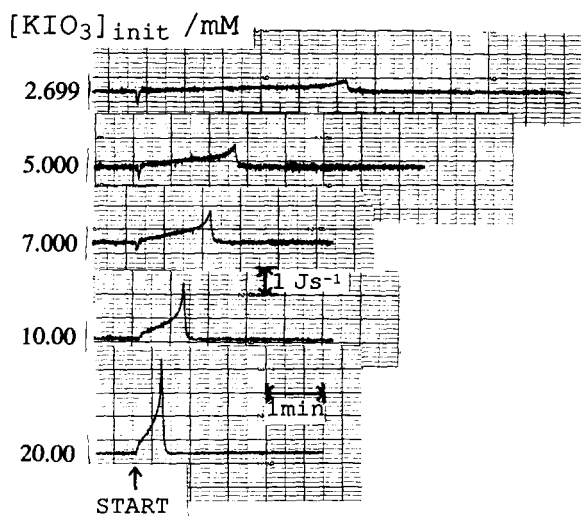


Fig. 3. Traces of  $q$  at several  $[\text{KIO}_3]_{\text{init}}$  observed in 3.84 mM  $[\text{NaHSO}_3]_{\text{init}}$ .

Heats of solution of sodium hydrogen sulphite crystals added to 50.0 g of water were measured separately. The sample size was varied from 10 and 40 mg, and the observed  $Q$  value was within the range 0.9–3.9 J. The mean value from 26 runs and the standard deviation (SD) were  $-96.0 \pm 1.2$  mJ per mg of sodium hydrogen sulphite in 50.0 g of water, and the heat of solution in water  $Q_{\text{sol}}$  was estimated to be  $-199.8 \pm 2.5$  kJ kg mol $^{-1}$  at  $25.0 \pm 0.1^\circ\text{C}$ .

Sodium hydrogen sulphite crystals of several sample sizes were added to vessel S containing 50.0 g of  $(5.000 \pm 0.001)$  mM potassium iodate solution. These concentrations are expressed as  $[\text{NaHSO}_3]_{\text{init}}$  and  $[\text{KIO}_3]_{\text{init}}$  in the present report. The observed traces of  $q$  are shown in Fig. 2. With an increase in  $[\text{NaHSO}_3]_{\text{init}}$ , the peak height of trace  $q$  increases and at the same time  $t$  decreases. Plots of  $t^{-1}$  vs.  $[\text{NaHSO}_3]_{\text{init}}$  were linear, as shown in Fig. 4, curve B. Each point is represented as the mean of five or six runs and the SD is shown by the length of the corresponding bar. In the last two cases, the time necessary for the colour change of a sample solution including starch was examined by a visual method. The results were also plotted on the same line as curve B.

The total heat effect  $Q$  corresponded to the area or the integrated value of the curve  $q$  over the baseline, and was observed easily in practice as the output of the operational amplifier. In the present work,  $Q_{\text{reac}}$  was obtained from the observed  $Q$  and  $Q_{\text{sol}}$ . The mean of  $Q_{\text{reac}}$  in J per 1 mg of sodium hydrogen sulphite was estimated from five or six runs at 5.000

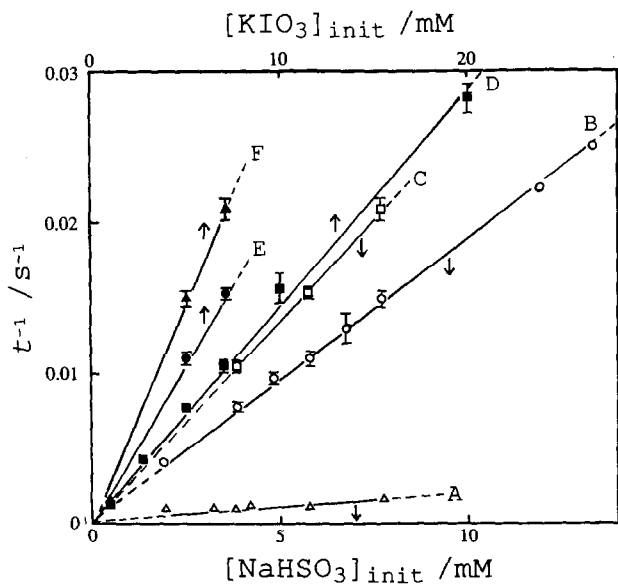


Fig. 4. Plots of  $t^{-1}$  vs.  $[\text{NaHSO}_3]_{\text{init}}$  in traces A, B and C shown with open symbols estimated at 1, 5 and 7 mM  $[\text{KIO}_3]_{\text{init}}$ , respectively, and plots of  $t^{-1}$  vs.  $[\text{KIO}_3]_{\text{init}}$  in traces D, E and F with filled symbols at 20, 30 and 40 mg of  $[\text{NaHSO}_3]_{\text{init}}$ , respectively.

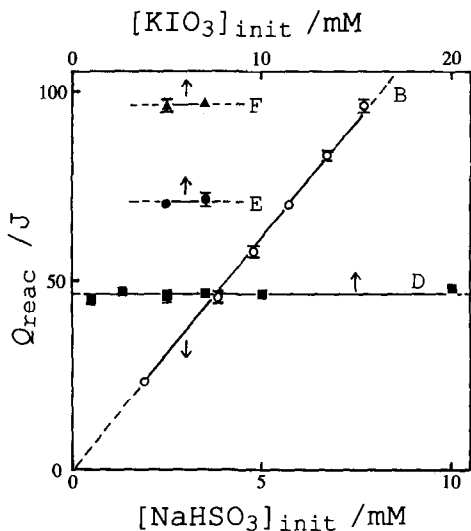


Fig. 5. Plots of  $Q_{\text{reac}}$  vs.  $[\text{NaHSO}_3]_{\text{init}}$  in trace B shown with open symbols estimated at 1, 5 and 7 mM of  $[\text{KIO}_3]_{\text{init}}$ , and plots of  $Q_{\text{reac}}$  vs.  $[\text{KIO}_3]_{\text{init}}$  in traces D, E and F with filled symbols at 20, 30 and 40 mg of  $[\text{NaHSO}_3]_{\text{init}}$ , respectively.

mM  $[\text{KIO}_3]_{\text{init}}$  to be 22.72(0.19), 45.11(0.98), 56.72(0.98), 69.08(0.60), 82.10(1.05) and 95.02(1.16) with the addition of sodium hydrogen sulphite crystals of weight 10 mg (or 1.92 mM), 20 mg (3.84 mM), 25 mg (4.80 mM), 30 mg (5.77 mM), 35 mg (6.73 mM) and 40 mg (7.69 mM), respectively. The SD values are shown in parentheses. Plots of these data were linear and the line B in Fig. 5 was calculated by the method of least squares to be  $Q_{\text{reac}} = 2.412[\text{NaHSO}_3]_{\text{init}} - 2.543$ .

In 1.000 and 7.000 mM solutions of  $[\text{KIO}_3]_{\text{init}}$ ,  $t$  values were observed at several  $[\text{NaHSO}_3]_{\text{init}}$  similarly, and are plotted in Fig. 4 as curves A and C, respectively. The plots of  $Q_{\text{reac}}$  vs.  $[\text{NaHSO}_3]_{\text{init}}$  in Fig. 5 fell on line B, the dilute solution being in the lower region of  $[\text{NaHSO}_3]_{\text{init}}$  and the concentrated solution near the middle. For example, means of  $Q_{\text{reac}}$ , in J, each obtained from four runs in aqueous  $[\text{KIO}_3]_{\text{init}}$  solutions of 7.000 mM were estimated to be 45.37(0.15), 70.65(0.87) and 95.83(0.68) for crystal weights of 20, 30 and 40 mg, respectively. The values of SD are again shown in parentheses.

Then sodium hydrogen sulphite crystals of weight 20 mg (corresponding to 3.84 mM) were added to 50.0 g portions of several potassium iodate solutions. The observed traces of  $q$  vs.  $t$  are shown in Fig. 3. With increases in the concentration of  $[\text{KIO}_3]_{\text{init}}$ , the peak height of trace  $q$  also increased, and  $t$  decreased. Plots of  $t^{-1}$  vs.  $[\text{KIO}_3]_{\text{init}}$  were linear, passing through the origin, as shown in Fig. 4 as curve D. However, plots of  $Q_{\text{reac}}$  vs.  $[\text{KIO}_3]_{\text{init}}$  were horizontally linear within the range of error, as shown in Fig. 5 as curve D. The mean values of  $Q_{\text{reac}}$ , in J, each estimated from

four runs were 46.19(0.38), 45.11(0.98), 45.37(0.15), 45.92(0.22) and 46.98(0.50) for potassium iodate solutions of 2.699, 5.000, 7.000, 10.000 and 19.999 mM, respectively. The calculated expression was  $Q_{\text{reac}} = 0.0778[\text{KIO}_3]_{\text{init}} - 45.27$ .

Similarly, sodium hydrogen sulphite crystals of weights 30 mg (5.77 mM) and 40 mg (7.69 mM) were added to  $[\text{KIO}_3]_{\text{init}}$  solutions of 7.000 mM. The observed values of  $t^{-1}$  and  $Q_{\text{reac}}$  were plotted against  $[\text{KIO}_3]_{\text{init}}$  in Figs. 4 and 5 as curves E and F, respectively. The values of  $Q_{\text{reac}}$  in Fig. 5 depended only on the sample size of sodium hydrogen sulphite. In the same manner, means of  $Q_{\text{reac}}$  (J) were 70.65(0.87) and 95.83(0.68) for weighed sodium hydrogen sulphite samples of 30 and 40 mg, respectively. It may be clearly seen from Figs. 4 and 5 that  $t$  and  $q$  depended on the concentrations of both sodium hydrogen sulphite and potassium iodate, but that  $Q_{\text{reac}}$  depended only on the concentration of sodium hydrogen sulphite, in spite of variation of the potassium iodate concentrations.

The heat of reaction  $\Delta H$  was estimated to be  $-239.9 \pm 5.5$  kJ per mole of sodium hydrogen sulphite at  $25.0 \pm 0.1^\circ\text{C}$ . Reactions (1) and (3), in which the species  $\text{HSO}_3^-$  is involved, may play an important role in the thermal behaviour.

In the literature [1, 2] it is reported that the clock reaction proceeds with an excess of iodate ions present. Excess of iodate ions was also necessary for occurrence of a colour change in the experiments involving the iodine–starch reaction. In reaction (1), and also derived from reactions (2) and (3),  $\text{HSO}_3^-$  may need three times as much  $\text{IO}_3^-$ , or  $[\text{NaHSO}_3]_{\text{init}} < 3[\text{KIO}_3]_{\text{init}}$ , as the starting concentration. Reaction (2) may also be necessary for the production of iodine to effect the colour change even though the clock reaction occurs in a total reaction of three steps. The requirement of stoichiometry for the colour change led to satisfactory results in obtaining the thermal signals. In the literature [7], the  $\Delta H$  of the  $\text{IO}_3^- - \text{I}^-$  reaction is  $+165.8$  kJ mol $^{-1}$  and the  $\Delta H$  of  $\text{HSO}_3^- - \text{SO}_4^{2-}$  is  $-283.1$  kJ mol. The  $\Delta H$  for reaction (1) was calculated to be  $-227.8$  kJ mol of  $[\text{HSO}_3^-]$  from these values, which approximated to the value in this report. The observed pH values, changed approximately from 5.4 to 2.6 and from 5.5 to 2.3 with the use of 20 and 40 mg of sodium hydrogen sulphite, respectively. In this pH region the species  $\text{HSO}_3^-$  may be dominant. However,  $\Delta H_{12}$  corrected to infinite dilution is 4.00 at  $25^\circ\text{C}$  [8]. If the heat of dissociation of  $\text{H}_2\text{SO}_3 - \text{HSO}_3^-$  is taken into consideration, the observed  $\Delta H$  may be  $-235.9 \pm 5.5$  kJ per mole of sodium hydrogen sulphite.

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