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The Kinetics of Zinc Dissolution in Nitric Acid

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The dissolution of zinc in 0.48–1.49 *M* HNO_3 was studied at 15–25 °C, by following simultaneously the concentration changes of the reactants (Zn and HNO_3), intermediate (HNO_2) and product (Zn^{2+}) with time. Explicit mechanisms were suggested for the dissolution of zinc in nitric acid. The kinetics of the dissolution process show that it is of the first-order with respect to [Zn] and [HNO_2]. The data obtained show that the dissolution process is diffusion-controlled. The mechanism of zinc dissolution is compared with the mechanism of copper dissolution.

(Keywords: Nitric acid; Nitrous acid intermediate; Zinc dissolution)

Die Kinetik der Auflösung von Zink in Salpetersäure

Die Auflösung von Zink in 0.48—1.49 *M* HNO_3 wurde bei 15—25 °C mittels gleichzeitiger Verfolgung der Konzentrationsänderungen der Reaktanden (Zn und HNO_3), des intermediären HNO_2 und des Produkts Zn^{2+} untersucht. Es wird ein Mechanismus vorgeschlagen. Die Kinetik der Auflösung ist erster Ordnung bezüglich [Zn] und [HNO_2]. Die Daten zeigen, daß der Auflösungsvorgang diffusionskontrolliert ist. Der Mechanismus der Auflösung von Zink wird mit dem der Kupferauflösung verglichen.

Introduction

An exhaustive survey of the available literature shows a paucity of experimental data on the dissolution of zinc in aqueous solutions of nitric acid. However, in the early work [1–4], and the subsequent work reported recently [5] about the electrochemical and chemical behavior of zinc in nitric acid solutions, attention has been paid to investigating the reaction products. It has been reported [2] that in 2% and 5% HNO_3, no HNO_2 is formed but an appreciable amount of HNO_2 formation is reported with 10% HNO_3. In dilute acid solutions, with concentration less than 25%

HNO_3, the products of the zinc dissolution process (loc. cit.) consist of NH_3 and NH_4NO_3. It has been reported also that zinc oxide (ZnO) is formed in acid solutions having concentration above 25% HNO_3 [1].

The complexity of the reaction of zinc with dilute nitric acid can be judged from the fact that the course of the reaction and the nature of the reaction products vary vastly with concentration of nitric acid [6]. The net ionic equations for the reported reactions are:

$$4\,Zn + NO_3^- + 10\,H^+ \rightarrow 4\,Zn^{2+} + NH_4^+ + 3\,H_2O \qquad (1)$$

$$4\,Zn + 2\,NO_3^- + 10\,H^+ \rightarrow 4\,Zn^{2+} + N_2O + 5\,H_2O \qquad (2)$$

$$4\,Zn + 2\,NO_3^- + 8\,H^+ \rightarrow 3\,Zn^{2+} + 2\,NO + 4\,H_2O \qquad (3)$$

In this study, it was the primary objective to investigate the kinetics of zinc dissolution in nitric acid on a quantitative basis by determining simultaneously the rate of consumption of the reactants and the rate of formation of the products, characterizing as far as possible the nature of the intermediates which participate in the reaction. The present work also includes the effect of the surface area of zinc, the concentration of nitric acid and temperature on the rate of Zn/HNO_3 reactions.

Experimental

Materials and Chemicals

a) Zinc Sheets: The (BDH grade) zinc sheets used in all the experiments were of various dimensions. A sheet of 50 × 40 × 0.38 mm was used in the general set of experiments. However, in the experiments dealing with the effect of surface area on the rate of dissolution, sheets of 50 × 30 × 0.38 and 50 × 20 × 0.38 mm were used.

b) Nitric Acid: Nitric acid of concentrations 1.49, 1.03 and 0.48 *M* were prepared by appropriate dilution of the (Analar grade) concentrated nitric acid. The prepared solutions were standardized using a standard sodium carbonate solution.

Determination of the Dissolution Rate

The zinc specimen was etched in HNO_3/H_2O mixture (3 : 1) for about 10 seconds, then thoroughly washed with distilled water and dried with a jet of air. This treatment was carried out immediately before starting the experiment. A 140 ml aliquot of the used acid solution was placed in a 250 ml beaker, high form, and thermostated at the ambient temperature using a *Griffin* regulated water-bath, accurate to ± 0.02 °C. The cleaned, weighed specimen was then taken and immersed vertically in solution stirred at a speed of about 1 000 revolution per minute using a *Gallenkamp* magnetic stirrer.

The change in concentrations of HNO_3, Zn^{2+} and HNO_2 were followed simultaneously by withdrawing 1.00 ml aliquot of the solution each time, using a pipette 1 ml : 1/100. The amount withdrawn was divided into three portions:

a) The first portion of 0.30 ml was used for the determination of HNO_3 concentration, using a standard 0.0125 *M* Na_2CO_3 solution.

b) The second portion of 0.30 ml was used for the determination of HNO_2 concentration by adding a known excess of 0.02 *M* Ce(IV) sulphate solution and titrating the excess of Ce(IV) against 0.01 *M* Fe(II) solution using sodium-diphenyl sulphonate as indicator [7].

c) The remaining 0.40 ml was used for the determination of Zn^{2+} complexometrically with 0.01 *M EDTA* solution using Erichrome Black T as the indicator [8]. The zinc solution was titrated until the colour changed from wine-red to blue.

In all experiments, the total variation in volume of solution did not exceed 10%. The change in volume after each withdrawal was considered in the concentration calculations.

The standard errors in these determinations were ± 1.0, ± 2.0 and ± 1.5% for HNO_3, HNO_2, and Zn^{2+}, respectively.

The Zn/HNO_3 interaction was followed until the edges of the zinc specimen were conspicuously noticeable or the nitric acid was consumed. The measurements were carried out at 15, 20, and 25 ± 0.02 °C.

Results and Discussion

Figs. 1, 2 and 3 represent the change in concentrations of Zn^{2+}, HNO_2 and HNO_3 with time during the dissolution of zinc in nitric acid solutions of different concentrations at 20 °C. An exponential behavior can be seen in all cases except for the high concentrations of nitric acid (1.49 and

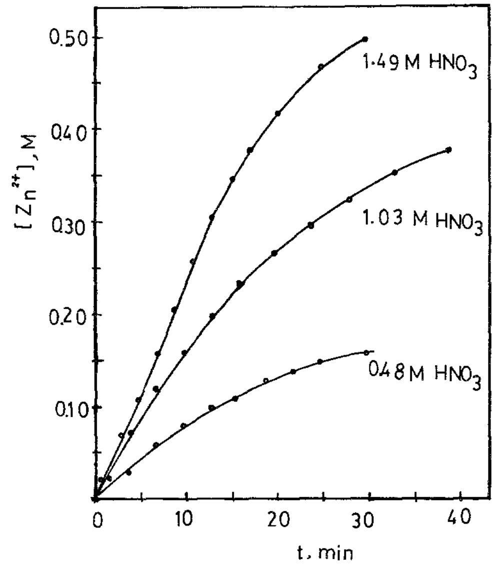

Fig. 1. The change in $[Zn^{2+}]$ with time in different nitric acid solutions at 20 °C; Zn surface area 40 cm^2

1.03 *M*) where the first part exhibits zero-order reaction. In the following, the behavior of zinc in 1.03 *M* HNO_3 is considered.

The plot of the logarithm of the formation rate of HNO_2 versus the logarithm of $[HNO_2]$ at two different concentrations of HNO_3, namely 1.49 and 1.03 *M*, gave straight lines with slopes with $n = 1.10$. This indicates that the formation of HNO_2 is of the first-order. In the same way, we found that the rate of zinc dissolution, as well as, HNO_3 acid consumption are first-order with respect to $[HNO_2]$.

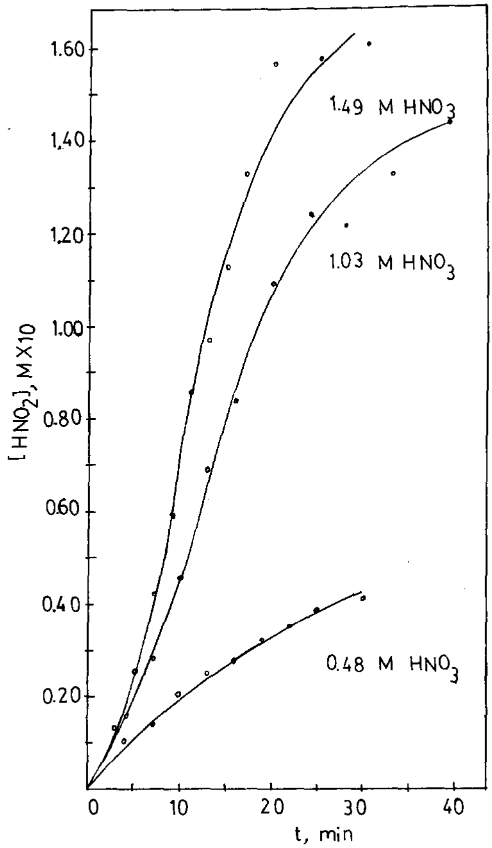

Fig. 2. The change in $[HNO_2]$ with time in different nitric acid solutions at 20 °C; Zn surface area 40 cm^2

Fig. 4 represents the change in $[Zn^{2+}]$ with time for different areas of zinc specimen in 1.03 *M* HNO_3 at 20 °C. The effect of surface area of zinc specimen on the rates of consumption of HNO_3 and formation of HNO_2

were also studied, and in these cases similar behavior was observed. We used the exponential part of the curves obtained for calculation of the rates. All the investigated rates were found to be directly proportional to the zinc surface area. This means that these rates are first-order with respect to [Zn]. The rates per unit surface area were also calculated, whereby comparable data were obtained (cf. Table 1).

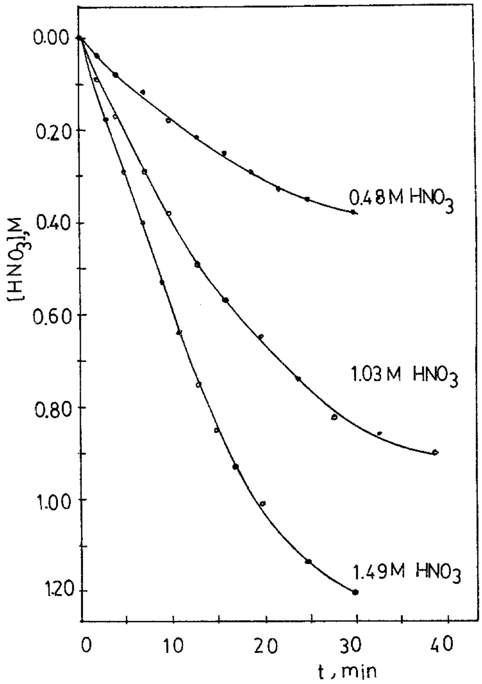

Fig. 3. The change in [HNO_3] with time in different nitric acid solutions at 20 °C; Zn surface area 40 cm^2

We conclude that the dissolution of Zn in HNO_3 acid has as the final products: Zn^{2+}, HNO_2 and NO gas, and it is a first-order reaction with respect to each of the reactants: Zn and HNO_3 and the products: Zn^{2+} and HNO_2. The formation of NO gas was confirmed by carrying the reaction in a closed tube partially filled with the HNO_3 acid solution. On opening the tube, dense brown fumes were instantaneously formed. The NO gas which escaped and was collected above the solution is readily oxidized to NO_2 gas by the oxygen of air.

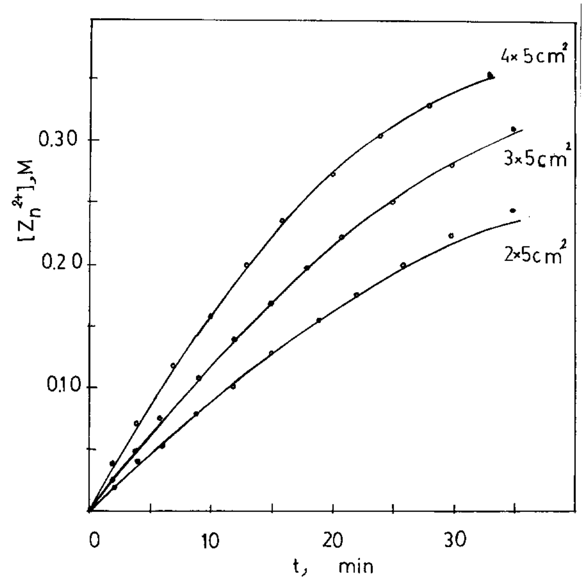

Fig. 4. The effect of surface area of zinc specimen on the dissolution rate of zinc in 1.03 *M* HNO_3 at 20 °C

Table 1. *The effect of zinc surface areas on: a) the dissolution rate of zinc, b) the formation rate of* HNO_2, *c) the consumption rate of* HNO_3; *in 1.03 M* HNO_3 *at 20 °C*

Rate	Surface area of Zn specimen, cm^2		
	20	30	40
a) The dissolution rate of Zn at $[HNO_2] = 0.06$ and $[HNO_3] = 0.58$ *M* in solution			
$\delta(Zn^{2+})$ mol min^{-1}	$6.25 \cdot 10^{-3}$	$8.57 \cdot 10^{-3}$	$1.20 \cdot 10^{-2}$
$\delta(Zn^{2+})$ mol min^{-1} cm^{-2}	$3.13 \cdot 10^{-4}$	$2.86 \cdot 10^{-4}$	$3.00 \cdot 10^{-4}$
b) The formation rate of HNO_2 at $[Zn^{2+}] = 0.17$ and $[HNO_3] = 0.61$ *M* in solution			
$\delta(HNO_2)$ mol min^{-1}	$3.00 \cdot 10^{-3}$	$4.67 \cdot 10^{-3}$	$5.72 \cdot 10^{-3}$
$\delta(HNO_2)$ mol min^{-1} cm^{-2}	$1.50 \cdot 10^{-4}$	$1.56 \cdot 10^{-4}$	$1.43 \cdot 10^{-4}$
c) The consumption rate of HNO_3 at $[HNO_2] = 0.05$ and $[Zn^{2+}] = 0.17$ *M* in solution			
$\delta(HNO_3)$ mol min^{-1}	$1.70 \cdot 10^{-2}$	$2.45 \cdot 10^{-2}$	$3.33 \cdot 10^{-2}$
$\delta(HNO_3)$ mol min^{-1} cm^{-2}	$8.50 \cdot 10^{-4}$	$8.17 \cdot 10^{-4}$	$8.33 \cdot 10^{-4}$

The following mechanisms, which have already been proposed [9] for copper dissolution in nitric acid, giving rise to the same reaction products, are also proposed for the formation of the zinc dissolution products. However, the experiments show that, although the zinc dissolution follows the same reaction mechanism as the one postulated for copper, the rates of the individual steps differ appreciably in the two cases:

$$Zn + NO^-_{3(ads)} + 3\,H^+ \rightarrow Zn^{2+} + HNO_2 + H_2O \tag{4}$$

$$Zn + HNO_2 + H^+ \rightarrow Zn^+ + NO + H_2O \tag{5a}$$

$$Zn^+ + HNO_2 + H^+ \rightarrow Zn^{2+} + NO + H_2O \tag{5b}$$

$$2\,NO + NO_3^- + H_2O + H^+ \rightarrow 3\,HNO_2\,[10] \tag{6}$$

As discussed in the case of copper dissolution (loc. cit.), the dissolution entails three steps: (i) The first step is the adsorption-desorption step (4), which is responsible for the initial formation of HNO_2 by reduction of the adsorbed NO_3^- on the zinc surface, it is very slow in the case of copper and is therefore the rate determining step. However, in case of zinc dissolution this step appears to be a fast one. This can be attributed to the difference in the electrochemical potential of zinc (-0.763 V) and copper ($+0.337$ V), according to which the zinc metal should be chemically more active than the copper metal. The relative ease with which zinc ions enter the solution from the metal and leave electrons behined on the metal accelerates the reduction of NO_3^- at the metal surface. (ii) The second step is related to the formation of Zn^{2+} and HNO_2; it is first-order with respect to $[HNO_2]$ and it is the rate determining step in case of zinc dissolution. Zn^+ is formed in step (5a), but since the monovalent state of zinc is highly unstable and strongly reductive [11], step (5b) will be very fast to form Zn^{2+}.

A step-by-step comparison with the mechanism of copper dissolution shows that the third step, which is zero-order with respect to $[HNO_2]$ in the case of copper dissolution, does not exist in the case of zinc dissolution, because of the excess of HNO_2, formed in the case of copper dissolution, is eliminated by the effect of stirring in the case of zinc dissolution.

Fig. 5 represents the effect of temperature on the dissolution rate of zinc in 1.03 M HNO_3. The temperature-dependence of the overall reaction rate expressed as $d[Zn^{2+}]/dt$, at constant values of $[HNO_3]$ and $[HNO_2]$, namely 0.45 and 0.08 M respectively, was investigated at 15, 20 and 25 °C. The plot of $\log d[Zn^{2+}]/dt$ versus $1/T$ gave a straight line. From the slope, $-E_a/2.303\,R$, a value of 13.03 $kJ\,mol^{-1}$ was calculated for E_a of the dissolution process. This value corresponds to a diffusion-controlled process. Thus, the stirring in the case of zinc increases the rate of dissolution by accelerating the diffusion of NO_3^- species from the bulk of solution to the metal solution interface, and the diffusion of the reaction products into the solution.

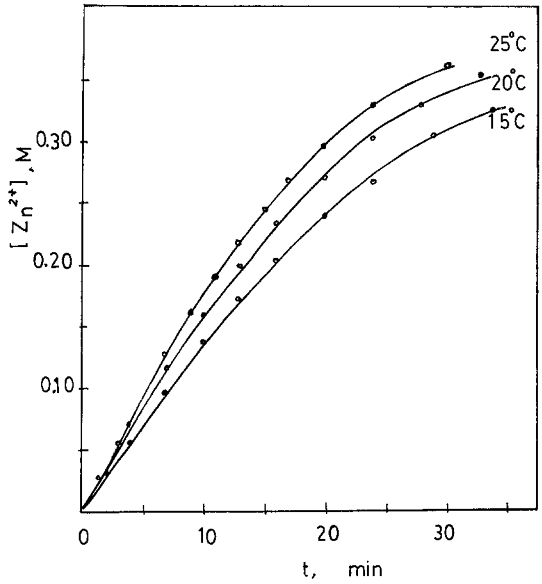

Fig. 5. The effect of temperature on the dissolution rate of zinc in 1.03 *M* HNO_3

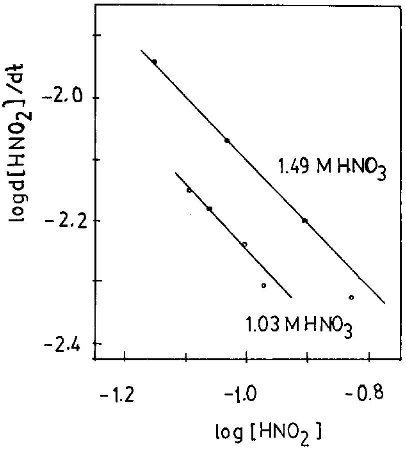

Fig. 6. Plot of the logarithm of the formation rate of HNO_2 versus log $[HNO_2]$ at 20 °C

Conclusion

It can be concluded from the results obtained that the dissolution of zinc in nitric acid is a first-order reaction with respect to the surface area of zinc, [Zn] and the concentration of [HNO_2]. Qualitatively speaking, the dissolution process of zinc in nitric acid follows the same mechanism as that for the dissolution of copper in nitric acid [9], except that in the case of copper the first step (adsorption-desorption) is the rate determining step, whereas in the case of zinc this step is very fast. On this basis the following mechanism for zinc dissolution may be advanced, including in addition to these steps, the adsorption-desorption step (4):

$$\mathrm{Zn} + \mathrm{NO_3^-} + 3\,\mathrm{H^+} \xrightarrow{k_0} \mathrm{Zn^{2+}} + \mathrm{HNO_2} + \mathrm{H_2O} \tag{4'}$$

$$\mathrm{Zn} + \mathrm{HNO_2} + \mathrm{H^+} \xrightarrow{k'} \mathrm{Zn^+} + \mathrm{NO} + \mathrm{H_2O} \tag{5 a}$$

$$\mathrm{Zn^+} + \mathrm{HNO_2} + \mathrm{H^+} \xrightarrow{k''} \mathrm{Zn^{2+}} + \mathrm{NO} + \mathrm{H_2O} \tag{5 b}$$

$$2\,\mathrm{NO} + \mathrm{NO_3^-} + \mathrm{H_2} + \mathrm{H^+} \xrightarrow{k'''} 3\,\mathrm{HNO_2} \tag{6}$$

In agreement with the difference in the behavior of the first step in the two cases, we found that the stirring brought about a stoppage of the copper reaction, whereas it resulted in the enhancement of the zinc reaction. This difference in behavior is due to the difference in the electrochemical potential of the metal copper and zinc.

The accumulation of HNO_2 in the case of copper is related to the higher concentration of HNO_3. It is 3.5 M in case of copper and 1.5 M in case of zinc as observed in the present set of experiments.

The rate equations can be written as:
The rate of Zn^{2+} formation is given by:

$$\mathrm{d}[\mathrm{Zn^{2+}}]/\mathrm{d}t = k_0[\mathrm{Zn}][\mathrm{NO_3^-}] + k''[\mathrm{Zn^+}][\mathrm{HNO_2}] \tag{7}$$

and the rate of Zn^+ formation can be expressed as:

$$\mathrm{d}[\mathrm{Zn^+}]/\mathrm{d}t = k'[\mathrm{Zn}][\mathrm{HNO_2}] - k''[\mathrm{Zn^+}][\mathrm{HNO_2}] \tag{8}$$

Since Zn^+ is a short-lived intermediate, we applied the steady state approximation ($\mathrm{d}[\mathrm{Zn^+}]/\mathrm{d}t = 0$). The application of the steady state approximation to equation (8) and rearranging gives:

$$[\mathrm{Zn^+}] = k'/k''[\mathrm{Zn}] \tag{9}$$

On substituting for [Zn^+] in equation (7):

$$\mathrm{d}[\mathrm{Zn^{2+}}]/\mathrm{d}t = (k_0[\mathrm{NO_3^-}] + k'[\mathrm{HNO_2}])[\mathrm{Zn}] \tag{10}$$

From the rate equations (4′) to (6), the overall rate of formation of HNO_2 is given by:

$$d[HNO_2]/dt = k_0[Zn][NO_3^-] + 3k'''[NO]^n[NO_3^-] - 2k'[Zn][HNO_2] \tag{11}$$

Similarly, the rate of NO formation can be expressed as:

$$d[NO]/dt = 2k'[Zn][HNO_2] - 2k'''[NO]^n[NO_3^-] \tag{12}$$

Since it was found experimentally (loc. cit.) that the rate of NO formation nearly equals its rate of consumption, one can write:

$$d[NO]/dt = 0 \tag{13}$$

Thus, equation (12) can be rearranged as:

$$[NO]^n = k'/k''' \frac{[Zn][HNO_2]}{[NO_3^-]} \tag{14}$$

Substitution of $[NO]^n$ in equation (11) and rearranging, gives:

$$d[HNO_2]/dt = (k_0[NO_3^-] + k'[HNO_2])[Zn] \tag{15}$$

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References

[1] *Zabolotny II* (1948) Poligraf Proizvodstov 1948: 5–9; Chem Zentr 1949: 1058

[2] *Leko AM, Radosavljević SD* (1947) Glasnik Khem Drushtva Beograd 12: 32–37

[3] *Leko AM, Radosavljević SD* (1948) Ibid 13: 90–95

[4] *Tadashi F* (1968) Tokyo Gakugei Daigaku Kiyo 19(2): 161–163

[5] *Semina EV, Sheberstov VI, Sorokoletova EI, Drozdova IG* (1978) Elektrokhimiya 14(6): 886–890

[6] *Vogel AI* (1965) Macro and semimicro qualitative inorganic analysis, 4th edn. Longman, p 292

[7] *Vogel AI* (1972) Quantitative inorganic analysis, 3rd edn. Longman, p 322

[8] *Vogel AI*, Ibid, p 433

[9] *El-Cheikh FM, Khalil SA, El-Manguch MA, Omar HA* (1983) Annali di Chimica 73: 75–89, by Società Chimica Italiana

[10] *Baranov AV, Pogrebnaya VL, Mal'chikova TV* (1970) Tr Krasnodar Politekh Inst 29: 179–185

[11] *Cotton A, Wilkinson G* (1980) Advanced inorganic chemistry, 4th edn. Wiley, Chichester, p 593