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COUPLING OF THERMOMETRIC TITRIMETRY AND CONSTANT-CURRENT COULOMETRY: STUDY AND APPLICATIONS

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Two systems involving the coupling of thermometric and coulometry are presented. In the first assembly, the two electrodes were in the same compartment. Bromocoulometry was used to test the possibilities of this coupling in the sequential titration of a vitamin C + aspirin mixture about (10^{-4} *M*) and the determination of enthalpy changes. In a second coupling system, the anodic and cathodic compartments were separated by a sintered-glass disc of porosity 3. The conditions for obtaining an electrochemical cell which is also a good calorimeter are discussed. Examples of applications are given, such as analytical measurements, the study of an electrochemically catalysed reaction and of the thermal effects of electrode reactions.

We describe here our first experiments on the coupling of constant-current calorimetry and thermometric titrimetry. The interest of this assembly is: for coulometry, thermometry is a new end-point method and allows access to thermodynamic data. For thermometry, coulometry presents two advantages: the first is the obtaining of unstable titrants such as Br_2, Ag^{2+}, O_2^- etc.; the second is the invariance of the heat capacity of the system, which facilitates calculations to obtain thermodynamic data.

This coupling has previously been applied only by Vajgand [1], fourteen years ago, to titrate weak bases in non-aqueous medium with end-point detection by "catalytic thermometric titration" [2], and very recently by Zsigrai and Bartusz [3] to titrate halides in molten salt, generating Ag^+ at 55°. In these two papers, the authors studied only the analytical aspects of this technique.

Many pharmaceutical substances are titrated by bromimetry [4], but bromine solutions are unstable. Bromine can be generated electrochemically; we have therefore chosen bromocoulometry to test our coupling system from analytical and thermodynamic aspects.

We have tested two coupling systems. In the first, the anodic and cathodic compartments were not separated. We shall give only the results here, for this study was described in a recent paper [5]. In the second system, the two compartments, were separated by a sintered-glass disc.

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Experimental

a – *Electronic material*

The temperature sensors were thermistors (VECO I.EA 31 A6 2B9); the voltage source, wheatstone bridge and operational amplifier were MacKee Pedersen instruments. The output voltage went either directly to an $E = f(t)$ recorder (Tacussel EPL 1 or Ecoscript) or to a highly sensitive millivoltmeter (Tacussel ISIS 20.000), which "digitalised" the signal and transferred it into a Hewlett–Packard HP 85 computer. The computer performed the different corrections: the effect of the stirrer, exchanges with the outside, the joule effect caused by the passage of current. Solutions were agitated by a four-blades glass stirrer, driven by a Tacussel "CONTROVIT" system, which has very good reproducibility. The potentiostat–galvanostat was a Princeton Applied Research 363.

b – *Calorimeters*

Three calorimeters were used. In the first coupling system (only one compartment) we used a simple round flask (100 ml) covered by aluminum paper and immersed in expanded polystyrene for analytical measurements, and the calorimeter was a Dewar flask built as recommended by Christensen for thermodynamic measurements [6]. The insert of the calorimeter was a 29–32 Teflon plug, through which the glass stirrer, the thermistor, a joule heat calibrator ($R = 100\ \Omega$), a titrant delivery tube and the electrodes were passed. These electrodes consisted of a 2 cm^2 platinum plate (working electrode) and a 1 cm long platinum wire 0.8 mm in diameter (counter electrode) with a distance of 3 mm between the two.

For the second coupling system (two separated compartments), the calorimeter was built from two hemispherical glass flasks, each of 100 ml volume. These two parts were separated by sintered-glass disc of porosity 3 (3 cm diameter) fixed with epoxy resin (araldite) glue and covered with aluminum paper (Fig. 1). This was all enclosed in a wooden box filled with polyurethane moss. The two R. I. N. served as the only openings in the box. The two inserts were symmetrical and as described above, except for the electrode. In this case it was a 6 cm^2 platinum trellis, placed correctly to arrive flat against the sintered-glass. When the current flowed, the joule effect was minimised by the large area of the sintered-glass junction and of the electrodes.

Study of the one-compartment system (system I)

a – *Specifications*

With 92 ml of water in the calorimeter, the overall heat capacity was 97.56 cal K^{-1}. The working and counter electrodes had different shapes, to minimise the reaction at the counter electrode of the products formed on the working electrode. We tested this

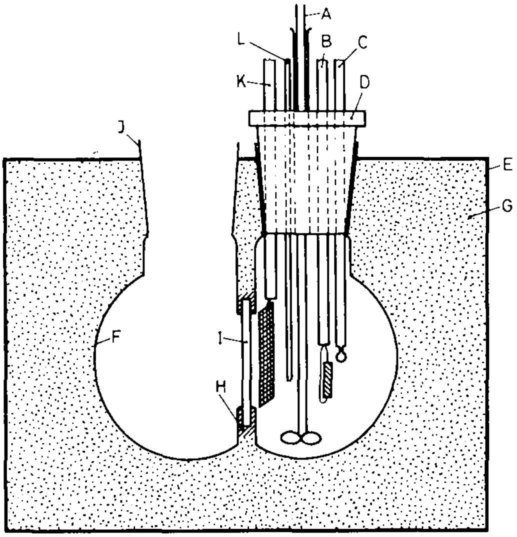

Fig. 1 Scheme of two-compartment system. A: stirrer, B: joule heat calibrator, C: thermistor, D: 29/32 teflon plug, E: Wooden box, F: glass flask covered with aluminum paper, G: polyurethane moss, H: epoxy resin glue, I: sintered-glass, J: 29/32 R. I. N., K: working electrode, L: ref. electrode or titrant or gas

point with the oxidation of a copper anode in 0.5 M H_2SO_4 ($i = 70$ mA during, 5, 10 and 15 min). Copper which was deposited on the cathode (platinum wire) was dissolved in concentrated HNO_3 and determined by atomic absorption spectrometry. We found 0.16, 0.66 and 1.5%, respectively. The cathodic deposit can be considered negligible, for the analysis time is generally less than 2 minutes.

b – *Results and discussion*

This system serves well for rapid analytical measurements, and this with a good accuracy.

1 – *Titration of vitamin C with Br_2*

The electrolyte was 0.5 *M* KBr in 0.5 *M* H_2SO_4. A current of 20 or 40 mA was used, depending on the final concentration. The reaction time was determined on the recorder. The results are expressed in % = i.t. 100/theoretical number of coulombs. Precision is represented by the standard deviation *s*. For 2, 5, 10 and 40×10^{-5} *M* vitamin C solutions, we found 99.3±3.9, 100.8±2.05, 101.2±1.5 and 99.8±1.6%, respectively.

2 – *Titration of a mixture of vitamin C and aspirin with Br_2*

Vitamin C reacts rapidly and completely with Br_2, whereas aspirin is brominated three times and the reaction takes place slowly. This allows the sequential titration of these two substances. Vitamin C was titrated first, and the production of Br_2 was continued until there was an excess. We waited one hour and titrated the bromine excess with a 0.1 *M* As(III) solution according to the usual technique of thermometric titrimetry. For a 4×10^{-4} *M* vitamin C and 2×10^{-4} *M* aspirin mixture, we found 3.98×10^{-4} and 2.01×10^{-4} *M*, respectively.

3 — *Determination of As(III)/Br_2 and vitamin C/Br_2 enthalpy changes*

For this experiment, the calorimeter was calibrated by "direct injection enthalpimetry" (mixing 0.5 ml of *M* NaOH with 92 ml of 2.5×10^{-3} *M* HCl). A 70 mA current was used, which gave a thermal power of 0.033 ± 0.008 J s^{-1} for Br_2 and H_2 electrochemical production and for the joule effect. We obtained 127.9 ± 2.1 and 129.2 ± 2.5 kJ mol^{-1}, respectively, for the enthalpy change of As(III) and vitamin C oxidation by bromine (Table 1). ΔH was determined by Barthel's triangulation method [7].

Table 1 Concentration and ΔH determinations with the two systems

System with	Substance	*n*	conc., *M*	Current, mA	% conc. ± s	$\Delta H \pm s$, kJ mol^{-1}
one compartment	Vitamin C	2	5×10^{-4}	70	99.8 ± 1.4	− 129.2 ± 2.5
	As(III)	3	5×10^{-4}	50	99.7 ± 0.5	− 122.0 ± 2.5
		2	5×10^{-4}	70	100.2 ± 0.7	− 127.9 ± 2.1
		2	10^{-3}	100	99.7	− 140.4 ± 0.1
two compartments	Vitamin C	2	2×10^{-3}	200	100.2 ± 0.2	− 132.8 ± 0.1
	As(III)	5	2×10^{-3}	200	101.0 ± 0.2	− 101.3 ± 1.2

Study of the two-compartment system (system II)

a — *Specifications*

Sintered-glass of porosity 3 is permeable. Thus, when 200 ml of a solution was placed in the calorimeter, it was divided, with 101.5 ml in the working compartment (C_w) and 98.5 ml in the counter compartment (C_c). This gives a heat capacity of 111.78 cal K^{-1} for C_w and 109.14 cal K^{-1} for C_c when the liquid was water, and 52.14 cal K^{-1} and 50.8 cal K^{-1} when the liquid was acetonitrile. There are two types of heat waste. The first is between the two compartments, through the sintered-glass, while the second takes place with the exterior. Figure 2 shows the temperature variations in C_w (curve 1) and C_c (curve 2). We can represent the temperature difference between the two compartments by the following equations [8], where P is the thermal power of the reaction, T_w, T_α, C_w and T_c, T_β and C_c are the temperature at time t, the temperature when the reaction stops, and the heat capacity in the working and counter compartments, respectively. χ_i is the inner heat transfer constant. During the reaction:

$$T_w - T_c = \frac{P}{\chi_i(C_w + C_c)}\left[1 - \exp\left(-\frac{\chi_i t(C_w + C_c)}{C_w}\right)\right] \tag{1}$$

After the reaction:

$$T_w - T_c = (T_\alpha - T_\beta)\exp\left(-\frac{\chi_i t(C_w + C_c)}{C_w}\right) \tag{2}$$

From Eq. (2) we can determine χ_i. The slope of the curve $\log(T_w - T_c) = f(t)$ is the same for water as for acetonitrile and gives $\chi_i = 7.0 \times 10^{-4}\ s^{-1}$ with a correlation coefficient $r > 0.999$ for 12 points.

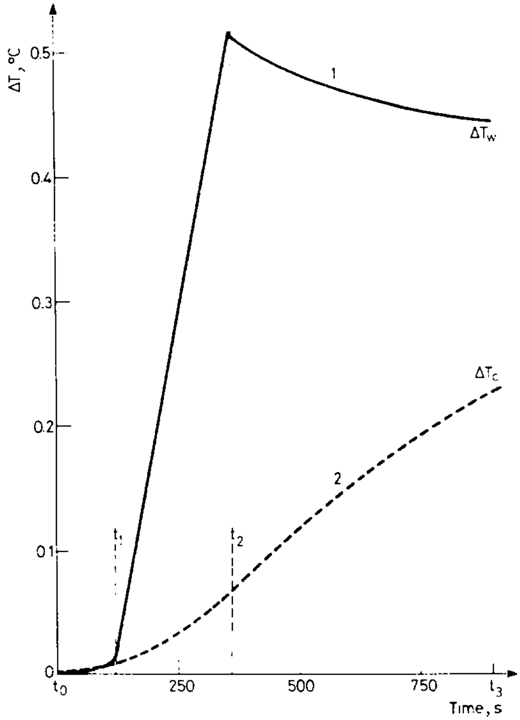

Fig. 2 Temperature change versus time in the two (working and counter) compartments for system II. t_0 to t_1: preperiod; t_1 to t_2: reaction period with thermal power P; t_2 to t_3: postperiod

To determine the outer heat transfer constant χ_0, we heated the two compartments at the same time with two joule heat calibrators. We obtained $\chi_0 = 8.0 \times 10^{-5}\ s^{-1}$ and an equilibration time of ≅ 3 minutes.

b — *Determination of an enthalpy change*

Before obtaining the results using Eqs (1) and (2), where ΔH is included in the term P and owing to the heat transfer between the two compartments, we tested 2 possibilities:

1. Reaction occurs only in the working compartment. When the reaction stops, the temperature decreases exponentially. Accordingly, the beginning of the curve was approximated to a straight line, and the curve was corrected with the aid of the usual Christensen method [9].

2. During the reaction, the counter compartment was heated with the joule heat calibrator, using the same thermal power as in the reaction, so that the two compartments were quasi-isothermal. The curve was corrected in the same way.

The results were equivalent ($\cong$ 1%).

c – *Applications*

1 – *Analytical results*

To avoid the diffusion of species from one compartment into the other, the same solution was put into the two compartments (however, when the concentrations were different in the two parts, tests showed that less than 1% of the species had crossed the sintered-glass after 20 minutes).

Titration of 2×10^{-3} *M* As(III) and vitamin C gave the same results as in system I: 101.0±0.1 and 100.2±0.2%, respectively. However, system I is more easy to manipulate and for analytical measurements we recommend this system.

2 – *Determination of As(III)/Br$_2$ and vitamin C/Br$_2$ enthalpy changes*

We wished to compare the results obtained with the two systems. Examination of Table 1 shows that the same ΔH was obtained for the oxidation of vitamin C by using bromine, while that of As(III) oxidation depended on the current. When a linear correlation was made between ΔH and i with the ΔH values obtained with system I, $\Delta H_0 = -102.8$ kJ mol^{-1} was obtained for $i = 0$ ($r = 0.996$), a value close to that obtained with system II (-101.3 ± 1.2 kJ mol^{-1}). Hydrogen is produced on the cathode. In system I, hydrogen can react with the oxidation product of the anodic

Table 2 Thermal effects ("ΔH") of electrode reactions

No.	Reaction	Salt	Medium	"ΔH", kJ mol^{-1}	R, Ω	r
1	$2\,Br^- \rightarrow Br_2$	0.5 *M* KBr	0.5 *M* H_2SO_4	−5.22	1.35	0.9994
2		0.5 *M* KBr	0.5 *M* H_2SO_4	−8.24	1.06	0.9992
3	$2\,Cl \rightarrow Cl_2$	0.5 *M* KCl	0.5 *M* H_2SO_4	−96.85	1.66	0.9997
4		0.5 *M* KCl	0.5 *M* H_2SO_4	−95.72	1.67	0.9963
5		0.5 *M* KCl	*M* KNO_3	−125.78	2.33	0.9985
6	$3\,I^- \rightarrow I_3^-$	0.5 *M* KI *	0.5 *M* H_2SO_4	−22.36	1.00	0.9984
7	$2\,H^+ \rightarrow H_2$		0.5 *M* H_2SO_4	−9.41	0.93	0.9867
8			0.5 *M* H_2SO_4	−15.32	1.38	0.9998
9	$2\,H_2O \rightarrow O_2$		0.5 *M* H_2SO_4	−312.66	1.08	0.9965

* unstable solution.

reaction. The oxidation product of vitamin C does not react with H_2, whereas As(V) reacts to give arsine (AsH_3). Through the rapid production of H_2 on the cathode, the effect of this system could be greater. In system II, As(V) cannot react with H_2 and we can take as "$i = 0$". If we put this ΔH value for "$i = 0$" in the previous linear correlation, we obtain $\Delta H_0 = -101.5$ kJ mol^{-1} ($r = 0.999$).

3 – *Determination of thermal effect of an electrode reaction*

When a substance is oxidized or reduced on an electrode, the temperature changes in the compartment. The heat change can be represented by the following expression:

$$Q = \frac{Ri^2t}{4.18} + \frac{it}{nF}\,''\Delta H'' \tag{3}$$

where Q and "ΔH" are expressed in calories, R is the resistance (in Ω) of the solution between the electrode and the sintered-glass, n is the number of electrons involved in the electrochemical process and F is the Faraday number. If this relation holds, the function $Q/i = f(i)$ must necessarily be a line whose slope allows determination of the solution resistance, and the intercept with the ordinate gives the enthalpy change. We electrolysed several salts during the time period t with current values of ±50, 100, 200 and 300 mA. Figure 3 shows the lines $Q/i = f(i)$ for the different products formed on the working electrode, and Table 2 gives the values of "ΔH" (kJ mol^{-1}), $R(\Omega)$ and the correlation coefficient r. Examination of r shows that we have actual lines.

What is the significance of this thermal effect? It is highly probable that it corresponds to the reaction (for example):

$$2\,Br^-_{\text{aqueous}} \xrightarrow{''\Delta H''} Br_{2\,\text{aqueous}} \tag{4}$$

and we have the cycle

$$\begin{tikzcd}
2\,Br^-_{\text{aqueous}} \arrow[r] \arrow[d, "\Delta H \text{ adsorption}"] & Br_{2\,\text{aqueous}} \\
2\,Br^-_{\substack{\text{adsorbed}\\ \text{on electrode}}} \arrow[r] & Br_{2\,\substack{\text{adsorbed}\\ \text{on electrode}}} \arrow[u, "\Delta H \text{ desorption}"']
\end{tikzcd}$$

It is difficult to link these results with the thermodynamic data, for in the Tables the heats of formation are relative and in these experiments we get absolute "ΔH". Moreover, the absorption and desorption energies are a function of the different ions present [10]. We can see this effect from the difference between "ΔH" for $2\,Cl^- \rightarrow Cl_2$ in 0.5 M H_2SO_4 and in M KNO_3.

Future experiments are necessary to explain these results. However, to our knowledge they are the first experimental results of this kind.

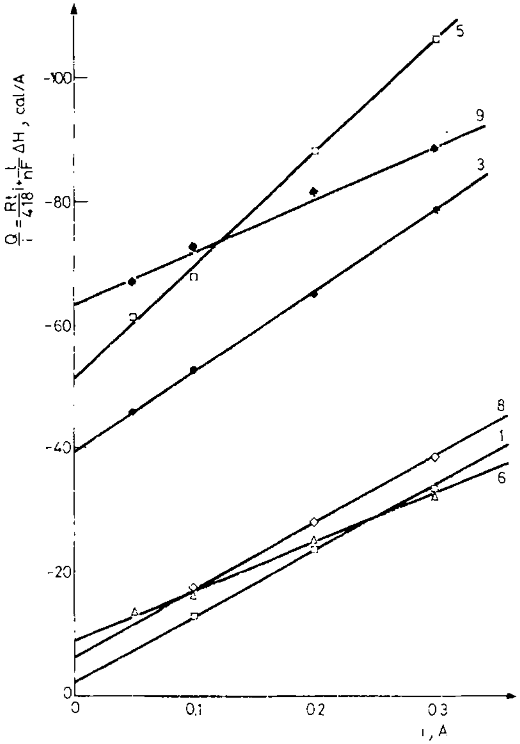

Fig. 3 Plots of $Q/i = f(i)$ (numbers correspond to those in Table 2)

4 — *Study of an electrochemically catalysed reaction*

In the previous section we saw that the thermal effect had two origins: the reaction and the joule effect. When the heat dissipated by the joule effect was too large compared with that of the reaction, the enthalpy change determination was difficult and inaccurate.

Generally, non-aqueous media are resistant; this gives a large joule effect. However, an electrochemical reaction that does not use current, for example a purely chemical reaction which is catalysed by electron transfer on an electrode, can be validly studied by thermometry, because the currents used are weak.

The reaction

$$\begin{aligned}&[(\eta^5 - C_5H_5)Fe^{II}(\eta^6 - C_6H_6)]^+ + 3\,P(OMe)_3 \rightarrow \\ &\quad\rightarrow [(\eta^5 - C_5H_5)Fe^{II}(P(OMe)_3)_3]^+\end{aligned} \tag{5}$$

occurs in $P(OMe)_3$ during 1 hour at 120°. The yield is very low. For these experimental conditions, no thermodynamic data for this reaction were available. However, through electron transfer catalysis [14] at ordinary temperature, this reaction is more feasible and has a good yield (100%) and our coupling system seemed well suitable for this study. Indeed, thermometry serves as a good technique to follow certain chemical reactions such as kinetic reactions [11–13].

Cyclic voltammetric study of this reaction [14] shows that it can be broken down into 4 steps in a solvent S:

$$\mathrm{cpFe^{+}Ar} + e^{-} \longrightarrow \mathrm{cpFeAr} \tag{6}$$

$$\mathrm{cpFeAr} + 3\,\mathrm{S} \longrightarrow \mathrm{cpFeS_3} + \mathrm{Ar} \tag{7}$$

$$\mathrm{cpFeS_3} + 3\,\mathrm{P(OMe)_3} \longrightarrow \mathrm{cpFe(P(OMe)_3)_3} + 3\,\mathrm{S} \tag{8}$$

$$\mathrm{cpFe(P(OMe)_3)_3} + \mathrm{cpFe^{+}Ar} \longrightarrow \mathrm{cpFeAr} + \mathrm{cpFe^{+}(P(OMe)_3)_3} \tag{9}$$

The first electron to produce cpFeAr was provided electrochemically. cpFeAr was again produced in a catalytic process according to reaction 9. Concurrently, we continued to produce it electrochemically to maintain the catalytic effect, for it decreased when the current was stopped (curve 8, Fig. 4: the induction current was curve $Q = f(t)$ rounded in place in the sharp break which showed the reaction end). The curve $Q = f(t)$ was concluded in the sharp break which showed the reaction end. The time at which the tangent at the end of the curve (dashed line, Fig. 4) intercepts the abscissa is called the "induction time". At present, we have not found an equation to

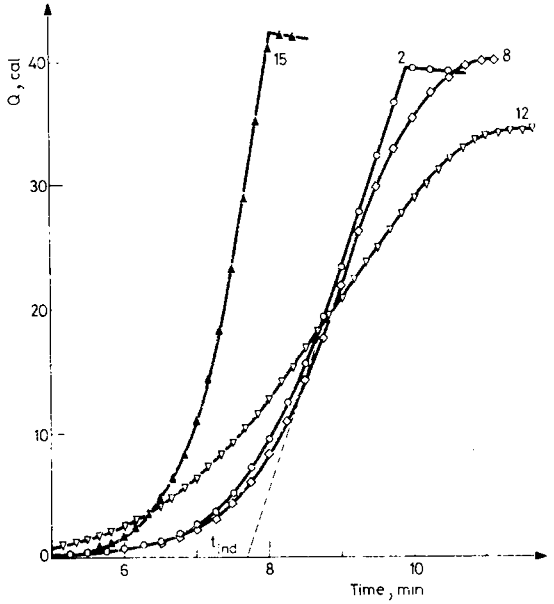

Fig. 4 Curves $Q = f(t)$ for different reactions $\mathrm{cpFe^{+}Ar} + 3\,\mathrm{P(OMe)_3}$ in doubly distilled $\mathrm{CH_3CN}$. Supporting electrolyte: 0.1 *M* tetrabutylammonium tetrafluoroborate. Numbers correspond to those in Table 3

Table 3 Study of reaction 4

No.	Arene	conc., cpFe$^+$Ar millimol l^{-1}	conc., P(OMe)$_3$ millimol l^{-1}	$\frac{\text{P(OMe)}_3}{\text{cpFe}^+\text{Ar}}$	i, mA	t_{ind} (a), min	ΔH, kJ mol^{-1}	$\Delta H \pm s$	"reaction rate" (a), 10^{6} mol s^{-1}
1	C_6H_6	20	120	6	− 10	6′45 6′20 (d)	− 197.7	− 199.0 ± 8.5	19.9 13.7 (d)
2		8	48	6	− 5	7′40	− 202.9		6.9
3		4	24	6	− 5	7′	− 198.7		4.8
4		8	48	6	− 10	7′20	− 215.2		10.8
5		8	24	3	− 5	10′40	− 192.5		6.3
6		8	16	2	− 5	11′30	− 184.5 (b)		4.5
7		8	16	2	− 5	11′	− 195.7 (b)		4.6
8		8	48	6	− 5 (c)	7′40	− 205.1		6.0
9	$p$$CH_3$–$C_6H_4$–$CH_3$	8	48	6	− 5		− 159.0	− 178.2 ± 14.4	
10		8	48	6	− 10	3′20	− 192.1		7.1
11		8	48	6	− 20	3′	− 185.6		11.7
12		8	48	6	− 5	6′30	− 176.1		3.2
13	CH_3O–C_6H_5	8	48	6	− 5	5′20	− 207.9	− 206.8 ± 6.7	10.1
14		8	48	6	− 10	10′20	− 194.6		13.1
15		8	48	6	− 5	4′	− 218.0		10.9

(a): induction time and "reaction rate" defined in text, (b) ΔH determined as $8 \times 10^{-3}/1.5$ mole reacted 3 P(OMe)$_3$ for 1 cpFe$^+$Ar, (c): the current was stopped when 50% of cpFe$^+$Ar had reacted, (d): value for concentration equivalent to 8×10^{-3} M. Electrolyte was 0.1 M $Bu_4N^+BF_4^-$ in CH_3CN.

describe the concentration variation of cpFe$^+$Ar against time; to a first approximation we shall take the slope of this "tangent" (in mol s^{-1}). We investigated the effects of the "induction current", cpFe$^+$Ar and $P(OMe)_3$ concentrations and arene substitutions. All results are given in Table 3 and represented in Fig. 4.

The thermometric study of an electrochemically catalysed reaction serves as a good supplement to the cyclic voltammetric study. In this way, we confirmed the results obtained with the latter method [14] on substituant effects. The working electrode potential recorded during the experiment gave the reduction potential of the initial or final products; they were the same as those found by voltammetry. The tests with 2 $P(OMe)_3$ for 1 cpFe$^+$Ar proved the stoichiometry of 3 $P(OMe)_3$ (the amount of cpFe$^+$Ar that reacted was one-third of the amount of $P(OMe)_3$).

From the thermometric study, supplementary information is available on what takes place in the bulk of the solution. Thus, we obtain the ΔH of the overall reaction and the way in which the product changes rate constant determination).

What is the significance of the ΔH difference between two different arenes? Is it the difference in bond energy between the metal and the ligand? This question was one of the purposes of studying this reaction, but it is too soon to draw conclusions at this point. The induction time seems more dependent on the ratio ($P(OMe)_3$)/(cpFe$^+$Ar) than on the induction current, but it is difficult to find a real relation. The final reaction rate is a function of the induction current, the concentration of reacting cpFe$^+$Ar and the arene substitution.

Conclusion

In this paper we have seen what can be obtained as new information when the thermometric and coulometric methods are coupled together. We believe that many other possibilities of analytical of thermodynamic studies involving these coupling systems remain to be discovered.

References

1 V. J. Vajgand, Talanta, 17 (1970) 415.
2 E. J. Greenhow, Chem. Rev. 77 (1977) 835.
3 I. J. Zsigrai and D. B. Bartusz, Talanta, 1 (1983) 54.
4 G. J. Patriarche, Labo Pharma Problèmes et Techniques, 280 (1978) 817.
5 P. Boudeville, J. L. Burgot and Y. Chauvel, Analusis, 11 (8) (1983) 406.
6 J. J. Christensen, R. M. Izatt and L. D. Hansen, Rev. Sci. Instrum., 36 (1965) 779.
7 J. Barthel, Thermometric Titration, John Wiley, New York, 1975, p. 27.
8 P. Boudeville and J. L. Burgot, in process works.
9 J. J. Christensen, R. M. Izatt, L. D. Hansen and J. A. Partridge, J. Phys. Chem., 70 (1966) 2003.
10 J. O. Bockris and A. K. Reddy, in Modern Electrochemistry, Vol. 2, Plenum Press, New York, 1970, p. 742.
11 P. Boudeville, J. L. Burgot and Y. Chauvel, Thermochim. Acta, 43 (1981) 313.
12 P. W. Carr, Crit. Rev. Anal. Chem., 2 (1972) 419.
13 P. Papoff and P. G. Zambonin, Talanta, 14 (1967) 581.
14 A. Darchen, J. Chem. Soc. Chem. Comm., (1983) 768.

Zusammenfassung — Zwei Systeme werden beschrieben, die eine Kombination von thermometrischer Titrimetrie und Coulometrie darstellen. Bei der ersten Vorrichtung sind die Elektroden im gleichen Raum Untergebracht. Die Bromocoulometric wurde zur Testung der durch diese Kombination für die aufeinanderfolgende Titration von Vitamin C/Aspirin-Gemischen (ungefähr 10^{-4} *M*) und für die Bestimmung der Enthalpieänderungen gebotenen Möglichkeiten angewandt. In einem zweiten kombinierten System waren Anoden- und Kathodenraum durch ein Sinterglasfilter der Porosität 3 voneinander getrennt. Es werden die Bedingungen diskutiert, die notwendig sind, um eine elektrochemische Zelle zu erhalten, die zugleich auch ein gutes Kalorimeter ist. Anwendungsbeispiele sind angegeben, wie analytische Messungen und elektrochemische Untersuchungen katalysierter Reaktionen oder thermischer Effekte von Elektrodenreaktionen.

Резюме — Представлены две системы, включающие связанные между собой установки для термометрической титриметрии и кулонометрии. В первой системе два электрода помещались в одной и той же камере. Бромокулонометрия была использована для проверки возможностей такого сочетания при последовательном титровании смеси витамин С + аспирин при концентрации около 10^{-4} *M* и определения изменений энтальпии. Во второй системе — анодная и катодная камеры были разделены диском из плавленного стекла и с пористостью №3. Обсуждены возможности изготовления электрохимической ячейки, являющейся также и хорошим калориметром. Приведены такие примеры ее применения, как аналитические измерения, изучение электрохимически катализируемой реакции или термических эффектов электродных реакций.