

TABLE 1.

P, r	$\delta, ^\circ\text{C}$	$\Delta T, ^\circ\text{C}$	$\Delta E, \text{cal g}^{-1}$	Deviation from ΔE_{av}
0.6928	0.0365	1.7855	6800.06	37.51
0.6747	0.0274	1.7384	6798.5	39.01
0.6103	0.0275	1.5885	6867.03	29.46
0.7111	0.0369	1.8380	6820.04	17.58
0.6242	0.0239	1.6219	6854.05	19.48
0.5808	0.0147	1.4587	6861.67	24.1
0.5675	0.0221	1.4711	6861.67	24.1
Mean			6837.51	± 26.89

TABLE 2.

P, r	$\delta, ^\circ\text{C}$	$\Delta T, ^\circ\text{C}$	$\Delta E, \text{cal g}^{-1}$	Deviation from ΔE_{av}
0.6581	0.0321	1.7461	7001.06	22.78
0.6969	0.0380	1.8510	7009.4	14.44
0.6413	0.0314	1.7114	7041.47	17.63
0.6095	0.0255	1.6245	7032.14	8.3
0.5590	0.0138	1.4908	7035.49	12.65
Mean			7023.84	± 15.2

of magnesium hydride was $6836.3 \pm 18.4 \text{ cal g}^{-1}$, practically identical with the earlier value of $6837.56 \text{ cal g}^{-1}$. In order to make sure that combustion had been complete, the solid products of combustion were analysed for the presence of magnesium hydride and metallic magnesium. No magnesium peroxide was detected among the combustion products, and hydration of the magnesium oxide had a negligible effect.

The relatively larger scatter in the results on heats of combustion, especially with the first specimen, is probably due to the fact that the weighed portion taken for combustion did not precisely correspond to the composition given by analysis; and even if it did, the variations in composition, which lie within the limits of accuracy of the analysis, may give an error of the order of 12 cal g^{-1} . This is confirmed by the far smaller relative error obtained with the purer specimen. After the necessary corrections have been made, the values obtained for ΔH_{298}° for the reaction $\text{MgH}_2 + \text{O}_2 = \text{MgO} + \text{H}_2\text{O}$ are -190.5 ± 0.9 and $-190.4 \pm 0.4 \text{ kcal} \times \text{mole}^{-1}$ for the first and second specimens respectively.

If the heat of formation of MgO is taken as $143.84 \text{ kcal} \times \text{mole}^{-1}$ ⁵ and that of H_2O as $68.317 \text{ kcal mole}^{-1}$ ⁵, the corresponding values obtained for the enthalpy of formation of magnesium hydride are -21.66 ± 0.9 and $-21.76 \pm 0.4 \text{ kcal} \times \text{mole}^{-1}$ respectively. The mean value obtained for the two specimens of magnesium hydride is $\Delta H_{298}^\circ = -21.71 \pm 0.65 \text{ kcal mole}^{-1}$, or $-90.83 \pm 2.72 \text{ kJ mole}^{-1}$.

The authors express their gratitude to Professor S. M. Skuratov for discussing the work.

SUMMARY

1. The heat of combustion of magnesium hydride has been determined.
2. The results have been used to calculate the enthalpy of formation of magnesium hydride.

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NON-POLAROGRAPHIC MAXIMA AT A DROPPING MERCURY ELECTRODE IN THE CATHODIC REDUCTION OF THE IRON-GROUP METALS

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The polarographic literature contains reports of non-polarographic maxima on current-potential curves, associated with the reduction of various organic compounds (oxidised forms or proton-donors) in the presence of inorganic and organic catalysts¹. The present paper examines the nature of a new type of non-polarographic maximum observed in the absence of organic compounds capable of cathodic reduction at a dropping mercury electrode.

We first observed such a maximum on polarographic curves in a study of the reduction of bivalent iron and nickel ions in $10 N$ calcium chloride in the presence of added tetrabutylammonium iodide. The character of the maximum on the $I-\varphi$ curves, the form of the corresponding $I-t$ curves, and the conditions for the occurrence of a maximum have been reported previously². It was then suggested that the observed non-polarographic maximum was due to the discharge of water molecules on iron or nickel microcrystals appearing on the surface of the dropping mercury electrode at the discharge potentials of their ions. If it is supposed that, within a definite range of sufficiently negative potentials (of the order of -1.5 V relative to the saturated calomel electrode, s.c.e.), desorption of tetrabutylammonium cations from the surfaces of iron and nickel microcrystals begins sooner than their desorption from a mercury surface, the possibility of such microcrystals remaining on the mercury surface can be explained, as well as the catalytic discharge of water molecules on them at these potentials.

The present paper represents an attempt to find experimental support for the hypotheses put forward earlier.

By analogy with the catalytic discharge of water observed in the reduction of Fe^{2+} and Ni^{2+} in the presence of tetrabutylammonium ions in $10 N \text{ CaCl}_2$, a similar effect can be

expected in the discharge of Co^{2+} ions. Fig. 1 (curves 1 and 2) shows polarographic curves of the reduction of Co^{2+} in 10 N CaCl_2 at a dropping mercury electrode alone and in the presence of tetrabutylammonium ions. Near the desorption potential of the latter (-1.54 V) a sharp current maximum is observed, the height and position of the peak depending on the concentrations of metal ions, supporting electrolyte, and tetrabutylammonium ions. With the supporting electrolyte more dilute than 5 N, a current maximum does not appear (with constant Co^{2+} and tetrabutylammonium concentrations). On further increase in the CaCl_2 concentration above 8–9 N the height of the maximum diminishes. In very concentrated solutions (of density 1.48) the maximum almost disappears, being highest in 8–9 N CaCl_2 . Fig. 2a illustrates $I-t$ curves corresponding to different points on the polarographic curve 2 in Fig. 1. They were recorded on a growing drop at constant potentials along the polarographic curves.

To prove the catalytic nature of the maxima, we have carried out analogous experiments on the reduction of Cd^{2+} and Zn^{2+} under conditions identical to those described above. Investigation of the cathodic reduction of these cations showed that in neither concentrated nor dilute solutions of the supporting electrolyte (CaCl_2) did the addition of tetrabutylammonium ions produce a maximum current on the $I-t$ curves like those observed in the reduction of iron, nickel, and cobalt. Figs. 2b and 2c illustrate $I-t$ curves for the reduction of Cd^{2+} and Zn^{2+} in 10 N CaCl_2 along the polarographic curve. No current maximum is evident, which is explained by the tendency of cadmium and zinc to be amalgamated and the high hydrogen overpotential on them. These facts provide good support for the earlier hypothesis that the maxima under investigation are catalytic in character².

As the reversibility of the reduction of iron, nickel, and cobalt ions is markedly increased in concentrated solutions of the halides owing to specific adsorption of halide ions², it was of interest to investigate the appearance of analogous

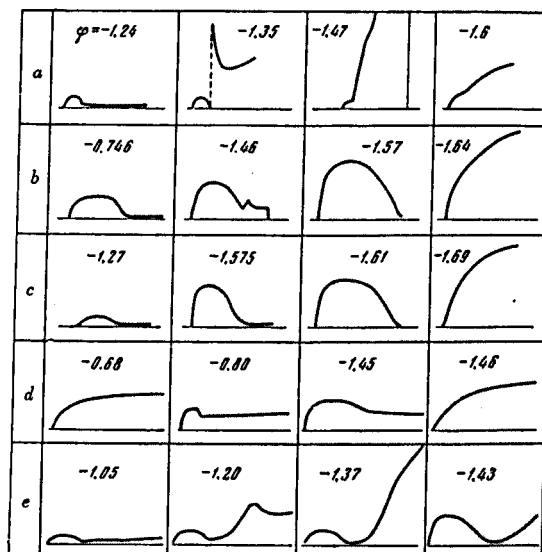


Fig. 2. Form of current-time curves, obtained before, at, and after the potential maximum (see Figs. 1 and 3), with a drop time of 6–8 s, in solutions of:

- a) 10 N CaCl_2 + Co^{2+} + tetrabutylammonium; b) 10 N CaCl_2 + Cd^{2+} + tetrabutylammonium; c) 10 N CaCl_2 + Zn^{2+} + tetrabutylammonium; d) 9 N LiCl + Ni^{2+} + tetrabutylammonium; e) 9 N $\text{Ca}(\text{ClO}_4)_2$ + Ni^{2+} + tetrabutylammonium.

maxima in concentrated solutions of lithium chloride and iodide (~9–10 N). The appearance of a maximum with lithium chloride as supporting electrolyte would make it possible to estimate the effect of specific adsorption on the catalytic discharge of water molecules. In order to compare results obtained in the presence of LiCl and LiI as supporting electrolyte with those obtained previously in CaCl_2 solutions, we have compared the influence of CaCl_2 and LiCl on the process. The experiments showed no fundamental difference between 10 N CaCl_2 and 10 N LiCl in the character of the polarographic reduction curves for the metals examined (see Fig. 1, curves 2 and 5). In both cases the addition of tetrabutylammonium ions is seen to produce arrests predominantly of diffusion character: the limiting current decreases, but the half-wave potential remains unchanged. The $I-t$ curves which we have obtained confirm that CaCl_2 and LiCl as supporting electrolytes have the same effect when at the same concentration.

Fig. 3 (curves 2 and 3) illustrates polarographic curves for the reduction of Ni^{2+} in 10 N LiCl with and without tetrabutylammonium ions present†. A characteristic feature of these curves is that small additions of tetrabutylammonium ions do not diminish the current at the beginning of the wave. Their retarding influence begins at potentials more negative than the zero-charge point of mercury in this

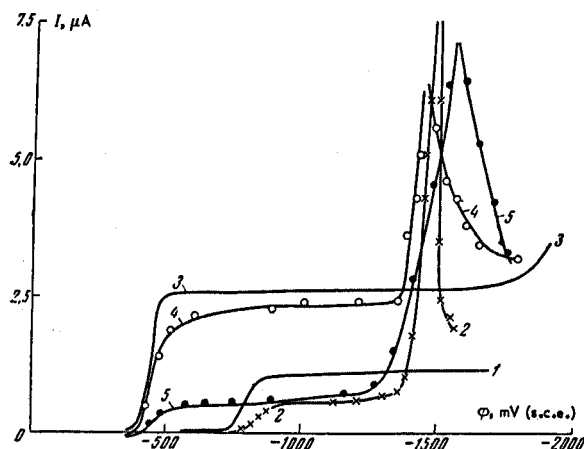


Fig. 1. Polarographic curves for the reduction of: 1) 0.001 M Co^{2+} in 10 N CaCl_2 ; 2) 0.001 M Co^{2+} in 10 N CaCl_2 + 0.0003 N tetrabutylammonium; 3) 0.003 M Ni^{2+} in 10 N LiCl ; 4) 0.0003 N Ni^{2+} in 10 N LiCl ; 5) 0.0003 N Ni^{2+} in 10 N LiCl + 0.001 N tetrabutylammonium.

† Concentrated solutions of lithium iodide were prepared by running a definite volume of twice distilled water into the cell, passing hydrogen through for 2–3 h, adding pieces of the fused salt LiI to the cell, and again passing hydrogen through. Only in this way could the oxidation of I^- to I_2 be avoided.

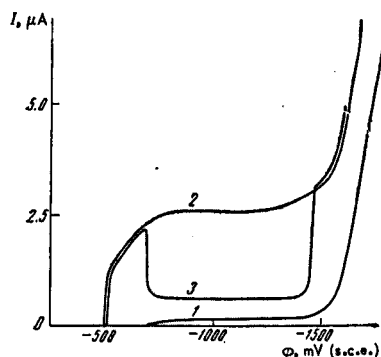


Fig. 3. Polarographic reduction curves obtained in solutions of:
1) 9 N LiI; 2) 0.003 N Ni^{2+} + 9 N LiI; 3) 0.003 N Ni^{2+} + 9 N LiI + tetrabutylammonium.

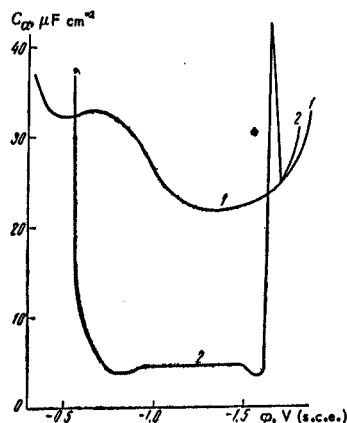


Fig. 4. Differential capacitance curves for mercury in: 1) 10 N CaCl_2 ; 2) 10 N CaCl_2 + 0.002 N tetrabutylammonium. [Neither Fig. 4 nor the actual curves seem to be mentioned in the text (Ed. of Translation).]

solution. Furthermore, the curves do not reveal the maximum which is well observed in CaCl_2 and LiCl solutions (cf. curve 3 in Fig. 3 with the curves in Fig. 1). The absence of a maximum is confirmed by the $I-t$ curves (Fig. 2d).

The shape of curve 3 (Fig. 3) between -0.4 and -1.3 V can be explained by the fact that, in concentrated lithium iodide solutions, the zero-charge point undergoes such a large negative displacement that adsorption of tetrabutylammonium ions becomes possible only at potentials more negative than -0.7 V. According to electrocapillary measurements which we have made, the zero-charge point of

mercury in 10 N CaCl_2 lies at -0.7 V (s.c.e.). It should obviously be at a more negative potential in lithium iodide solution of the same concentration.

As far as -0.7 V, iodide ions are adsorbed preferentially on the mercury surface, these increasing the reversibility of the discharge of metal ions. As far as -(0.5-0.6) V, therefore, the $I-\phi$ curve is unaffected by the presence of tetrabutylammonium ions. At more negative potentials the double layer undergoes a rearrangement³, and tetrabutylammonium ions begin to be adsorbed preferentially on the mercury surface, these retarding the discharge of metal ions with a sharp drop in current (cf. curves in Fig. 2d). Near -1.5 V the current rises to the limiting value as a result of desorption of the tetrabutylammonium ions. A catalytic maximum was not observed at these potentials.

The disappearance of the maximum in lithium iodide solutions can be explained on the basis of results for the desorption of tetrabutylammonium ions in iodide solutions, which in the case of a mercury electrode occurs⁴ within a narrow potential range, of 1-2 mV. Thus no region of gradual desorption of tetrabutylammonium ions can be observed on the $I-\phi$ curves: it is sufficient to change the potential by 1-2 mV for the mercury surface to be practically cleared of tetrabutylammonium ions. This phenomenon can be regarded as the reason for the absence of a maximum.

Our hypothesis was supported by experiments in saturated (~ 9.2 N) calcium perchlorate solution. Perchlorate ions possess a considerably smaller specific adsorption than chloride ions, and therefore a more extended range of desorption and a higher maximum were to be expected — and were found — in this solution than in CaCl_2 or LiCl solution (see Fig. 2e).

Measurement of the differential capacitance of the double layer on pure cobalt in potassium chloride solutions, carried out at our request by Wei Pao-ming with the aim of determining the desorption potential of tetrabutylammonium, showed that addition of the latter to these solutions produced a slight decrease in capacitance and very little increase in the hydrogen overpotential. This indicates that the adsorption of tetrabutylammonium cations on cobalt is insignificant, and that the discharge of water molecules is not greatly retarded in their presence. Hence tetrabutylammonium cations have practically no adverse effect on the catalytic action of the cobalt microcrystals present on the surface of a mercury electrode at the discharge potential of cobalt ions.

SUMMARY

1. The position and size of the peaks on the polarographic curves for reduction of the cobalt(II) ion depend on the concentrations of metal ions and supporting electrolyte, and on the presence of tetrabutylammonium.
2. The observed maxima are catalytic in character.
3. In solutions of the nickel(II) ion the retarding action of tetrabutylammonium begins at potentials more negative than the zero-charge point of mercury in this solution. The position of the zero-charge point depends on the supporting electrolyte.

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THERMOSTAT FOR EXPERIMENTS ON NUCLEAR MAGNETIC RESONANCE

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A peculiarity of the thermoregulation of specimens placed in the measuring head of instruments for the observation of nuclear magnetic resonance by the nuclear induction method, and also of those placed in the measuring head of a spin echo apparatus¹, is the impossibility or great complexity of using liquid heat-transfer media. The cause of these difficulties is that the test specimen is located in the induction coil of a resonance or aperiodic circuit, whose proper oscillations are much more strongly damped in the presence of a thermostating liquid, especially on direct contact with the latter, so that observation of the unknown effect becomes impossible. Liquids of low dielectric constant and dielectric losses are employed in some cases, but the danger then arises of dissolution, breakdown, or weakening of insulating coatings, etc. All this results in design complications from the introduction of protective devices for the oscillating circuits and other high-frequency apparatus.

It is most convenient to use gases or vapours as heat-transfer media when high-frequency fields are present. An arrangement for the thermoregulation of specimens in experiments on the observation of spin echo is reported below for the apparatus which we have described previously². The temperature of the test solutions is maintained at a specified value between 40° and -30°. Fig. 1 shows a block diagram of the equipment. Gaseous nitrogen is employed as heat-transfer agent, its rate of flow being regulated by control of a heater placed in the Dewar flask and connected to the mains through isolating and regulating autotransformers. In order to diminish the consumption of nitrogen and achieve lower temperatures, the measuring head with the specimen, through which the stream of nitrogen is blown, is separated by an air gap from the poles of the electromagnet, these being further cooled by cold water flowing through a coil of tubing placed over them. A

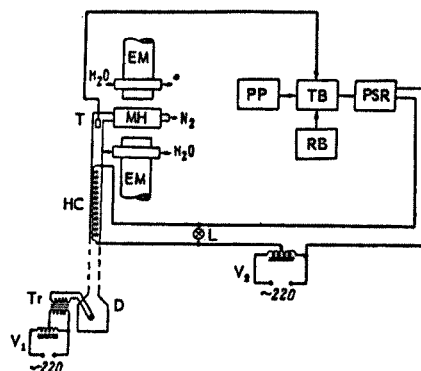


Fig. 1. Block diagram of thermoregulation of measuring head in spin echo apparatus¹: MH) measuring head; D) Dewar vessel containing liquid nitrogen; EM) electromagnets; HC) heating coil; T) thermistor; L) pilot lamp; RB) resistance box; PSR) regulating potentiometer; V₁) and V₂) regulating autotransformers; Tr) isolating transformer; TB) thermistor bridge; PP) power pack.

specified temperature is automatically maintained to within ± 0.01 deg by means of a device consisting of a thermistor bridge (Fig. 2) and a PSR-1-0.1 regulating potentiometer. Apart from the actual thermistor R_1 , which forms in the regulating device the transducer sensitive to the temperature of the stream of nitrogen, the bridge comprises the following units — resistance box R_2 , resistances R_4 and R_5 (forming the arms of the bridge), the potentiometer R_3 in the diagonal of the bridge, and the valve V. The thermoregulator cut-off is adjusted by varying the resistance R_2 in the box. The thermistor bridge is thus brought out of balance, and the resulting voltage applied to the regulating potentiometer PSR-1-0.1, the sensitivity of which can be controlled by means of the potentiometer R_3 . The PSR-1-0.1 is connected up in such a way that the contact group connected to the heating coil of the heat-exchanger is switched on when the temperature of the thermistor is below the specified value, and is switched off when the threshold temperature is reached. The stream of nitrogen flows around the heating coil, which extends along a glass tube (about 50 cm long and 8 mm in diameter) covered on

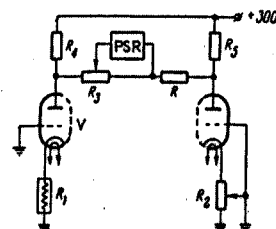


Fig. 2. Fundamental circuit of thermistor bridge.