

## POTENTIALS OF METALS IN MOLTEN POTASSIUM BISULPHATE\*

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**Abstract**—The galvanic behaviour of various metals in molten potassium bisulphate has been investigated, using a hydrogen reference electrode at 260–280°C. A galvanic series is presented to indicate the probable direction of galvanic effects in corrosion cells.

**Résumé**—Recherches sur le comportement galvanique de divers métaux dans  $\text{KHSO}_4$  fondu, avec une électrode de référence à hydrogène, entre 260–280°C. Une série galvanique est présentée en vue d'indiquer la direction probable des effets galvaniques dans les cellules de corrosion.

**Zusammenfassung**—Das galvanische Verhalten einiger Metalle in geschmolzenem Kaliumbisulfat unter wurde unter Verwendung einer wasserstoff-Referenzelektrode bei Temperaturen zwischen 260–280°C sucht. Die aufgestellte galvanische Reihe lässt auf die wahrscheinliche Richtung der galvanischen Vorgänge in Korrosionszellen schliessen.

BEFORE the discovery of a hydrogen reversible electrode at high temperatures,<sup>1</sup> a stable reference electrode was required for studying the electrochemical formation of hydrogen during the electrolysis of molten potassium bisulphate.<sup>2</sup>

After attempting to use various reference electrodes, we observed that when silver metal was dipped into the potassium bisulphate melt, a reproducible potential was obtained which was so stable that it could be used as reference to observe the variation of the potential of a working electrode in an electrolysis cell. The potential reached better stability sooner if silver ions were present initially in the melt. The stability was verified after the hydrogen reversible electrode was found; in fact, kinetic studies about hydrogen evolution were satisfactorily reproduced independently of the type of reference electrode employed.

The behaviour of other metals was different from that observed in the case of silver. The potentials cannot be ascribed to a metal/metal ion electrode properly. Consequently, as part of the investigation of molten potassium bisulphate electrochemistry, we have studied different metals in this melt using the hydrogen electrode as the reference electrode. All potentials reported are referred to it.

### EXPERIMENTAL TECHNIQUE

A Pyrex glass cell was used (Fig. 1). It consisted essentially of a round-bottom container with two electrodes, one the hydrogen reference electrode saturated with pure hydrogen at 1 atm (HRE) and another formed by a piece of metal attached to a copper wire. The cell had also an inlet tube to saturate the electrolyte with hydrogen. Experiments carried out in the range 260–280°C.

The following metals were tested; iron (Merck Darmstadt), nickel, cobalt (Johnson Matthey); lead (Coleman & Bell), copper and aluminium (electrolytic quality), silver

\* Manuscript received 27 July 1965.

(grade 1000), zinc, cadmium and magnesium (Merck, Darmstadt). Metals were used in the form of rods, wires or ribbons. The apparent area of electrodes was of the order of  $1 \text{ cm}^2$ .

Each piece of metal was properly cleaned and polished with different abrasives of progressive size and degreased. The electrode was placed in the cell without dipping it in the electrolyte whilst hydrogen was flushed through this for several min; the electrode was allowed to attain the temperature of the electrolyte.

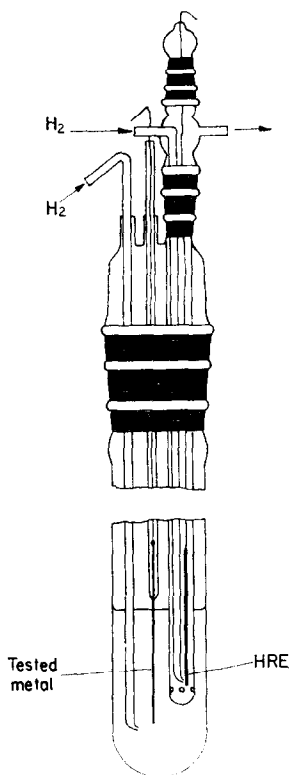


FIG. 1. Scheme of the cell.

Initially, the atmosphere of the cell was filled with purified nitrogen and later the electrolyte and reference electrode were saturated with purified hydrogen, which was flushed through the reference electrode continuously during each run.

The initial potential between the electrodes having been read, the metal electrodes were activated by means of pulses of current density ranging from  $10^{-5}$  to  $10^{-3} \text{ A/cm}^2$ , applied from a galvanostatic circuit. The duration of the pulses depended on the metal. The potentials of the electrodes were continuously recorded from the beginning of the experiments.

When silver, zinc and lead were used, different quantities of silver sulphate, zinc sulphate and lead sulphate were added to the electrolyte, at various concentrations of the order  $10^{-2} \text{ mol/1000 g}$  of melt, apart from the measurements done with pure potassium bisulphate.

## RESULTS

The evolution of the electrode potential for various metals is shown in the figures. Different electrodes, after a certain time, reached a constant potential independent of the pulses applied to the system. In general, these potentials show the characteristics of a steady mixed potential, as for the corrosion of metals in some aqueous systems.

The ionic species of the metals could be detected in the melt after the experiments and the surface of different metals presented characteristic patterns of corrosion.

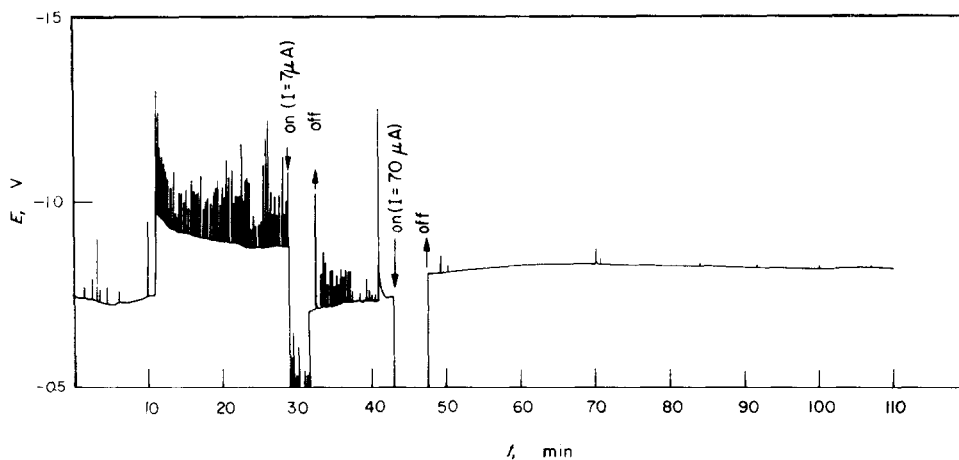


FIG. 2.  $E/t$  diagram for aluminium. 262°C.

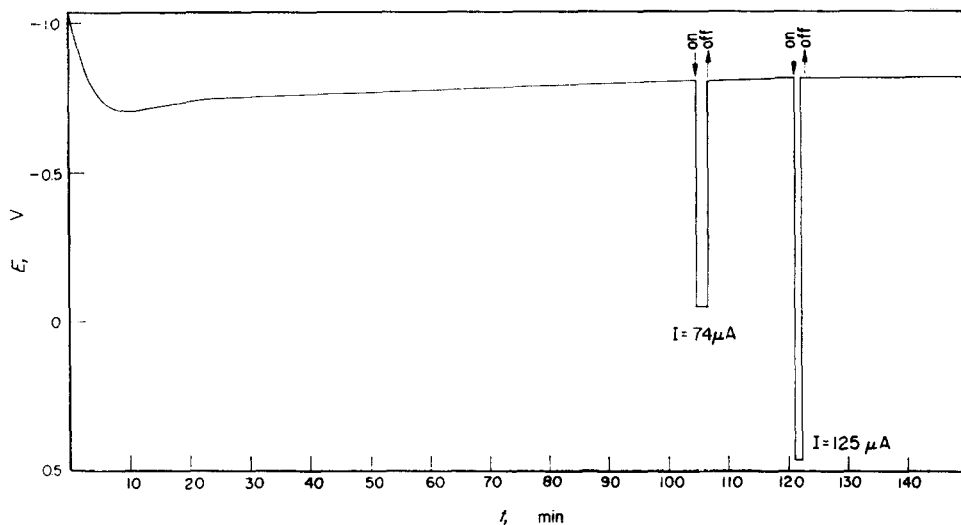


FIG. 3.  $E/t$  diagram for cadmium. 268°C.

*Aluminium.* This metal (Fig. 2) reaches its final potential very slowly. Usually the initial potential is not steady. The instability of the electrode potential is shown in the figure. The metal shows a tendency to acquire a very negative potential, as if an insoluble film were continuously formed and dissolved on the surface.

The same effect is observed if positive polarization is applied. A steady electrode

potential is obtained after 1 h from the beginning of the experiment. The final potential is  $-630 \pm 20$  mV. Even when this steady potential is reached, the metal still has a tendency to become more negative, as shown in the sharp peaks of the potential/time curve.

**Cadmium.** Cadmium shows interesting behaviour (Fig. 3). Initially, the electrode potential rises in the positive direction rapidly, and then after 10 min or thereabouts begins to decrease and reaches a final steady value after approximately 2 h. This final value is  $-820 \pm 10$  mV.

**Cobalt.** Here (Fig. 4) a small initial increase is observed; a maximum is reached after 3 min. The electrode potential then falls to  $-455 \pm 5$  mV after 35 min. The dissolution of the metal was observed in the melt.

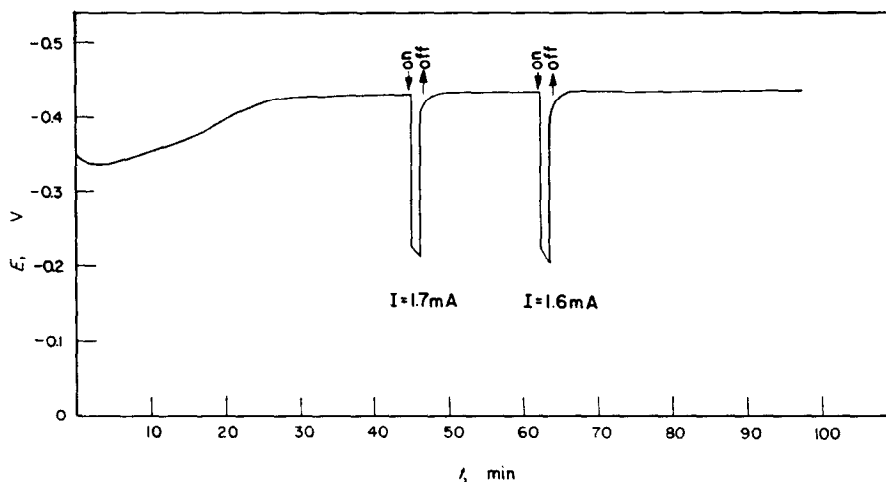


FIG. 4.  $E/t$  diagram for cobalt.  $268^{\circ}\text{C}$ .

**Copper.** The electrode potential of copper (Fig. 5) is steady; it reaches  $-550 \pm 10$  mV after each positive pulse, in less than 10 min. Rapid dissolution of the metal was observed.

**Iron.** Iron exhibits a very negative potential for a short time (Fig. 6) but this potential is not steady; it rapidly moves to the first step around  $-340$  mV and finally after 2 min reaches  $-200$  mV and finally stabilizes at  $-205 \pm 10$  mV after about 5 min. The metal shows a rapid response to positive pulses; when the pulses cease, it goes back the steady value in a few s.

**Lead.** The behaviour of this metal is rather complicated (Fig. 7). After falling to below  $-1000$  mV, in about 20 min it rises slowly to  $-650$  mV. About 50 min later, it falls to  $-845$  mV, finally reaching a steady value of  $-830 \pm 5$  mV. These facts can be attributed to the build up of an initial lead sulphate layer; the electrode was covered with insoluble lead sulphate.

**Magnesium.** Magnesium reaches a constant potential (Fig. 8) after having been immersed in the melt for about 20 min. When positive pulses are applied to the electrode a steady current flows, but when the current is interrupted the electrode potential moves to  $-1240$  mV and thereafter increases in a few min to the steady value of  $-1210 \pm 5$  mV.

**Nickel.** Initially the behaviour of this metal (Fig. 9) is similar to that of cobalt; a

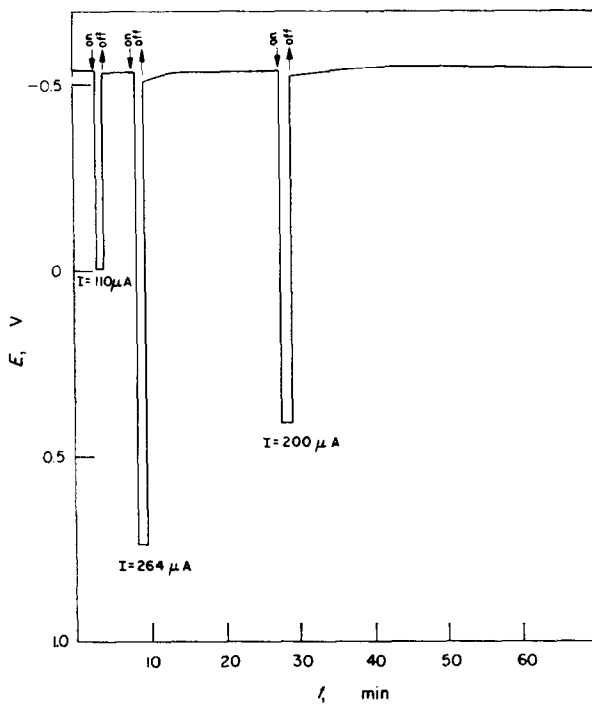


FIG. 5.  $E/t$  diagram for copper. 272°C.

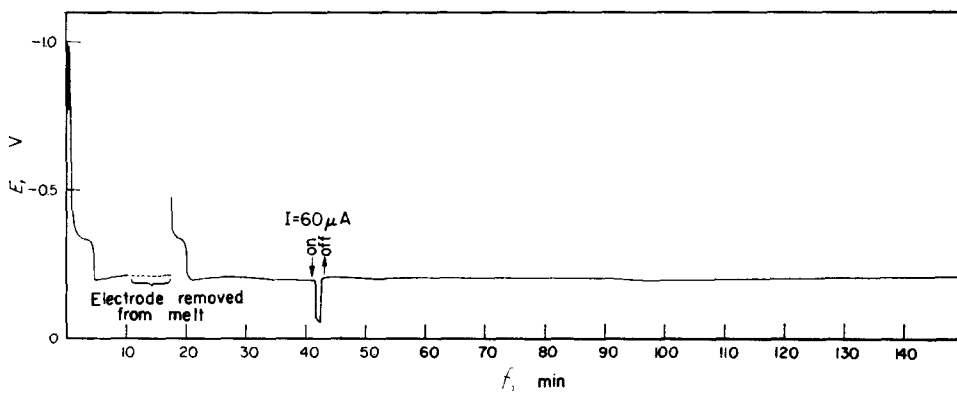
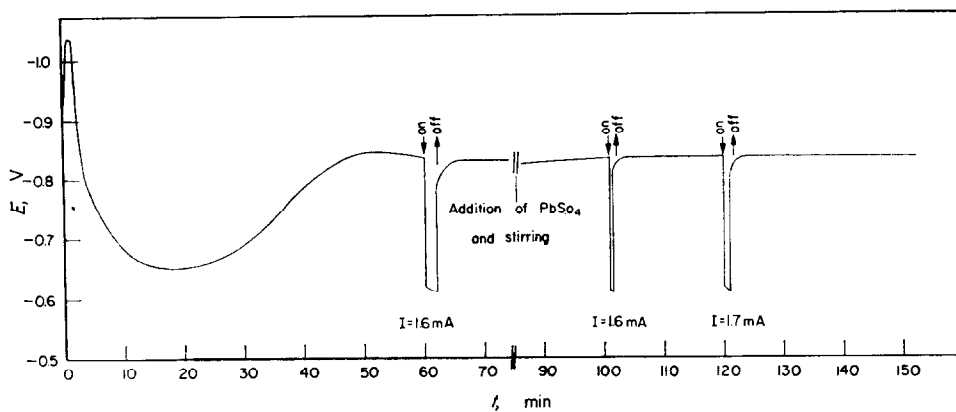
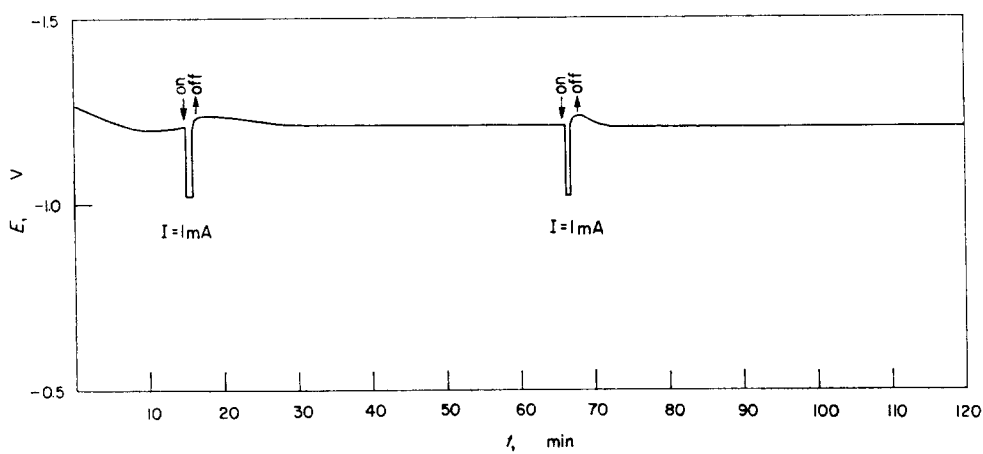
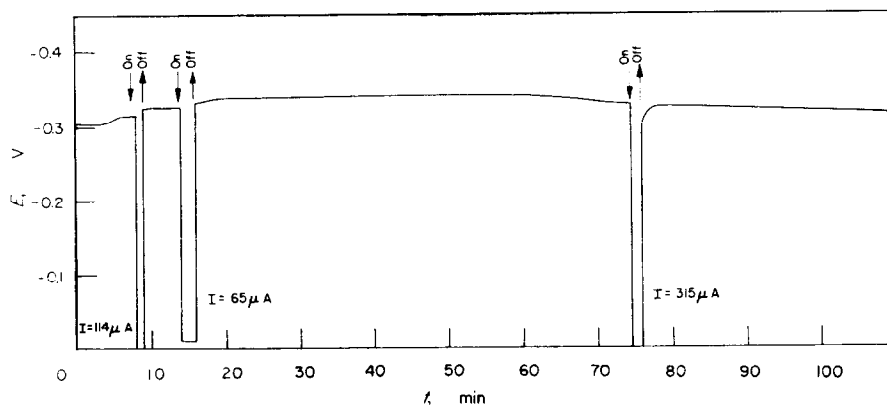
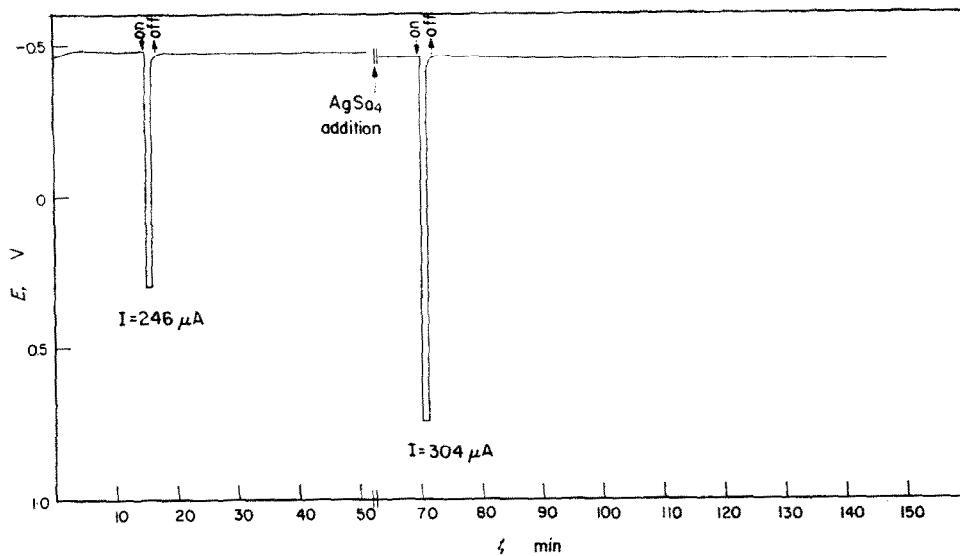
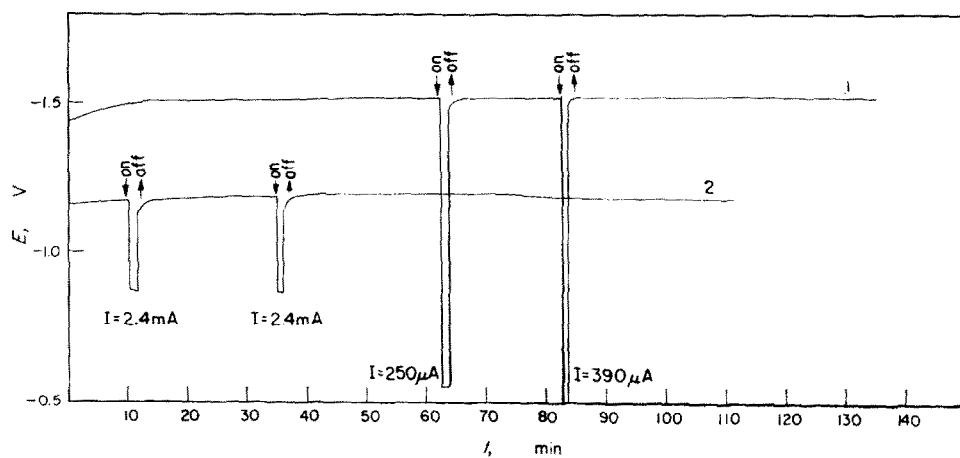


FIG. 6.  $E/t$  diagram for iron. 257°C.

FIG. 7.  $E/t$  diagram for lead. 278°C.FIG. 8.  $E/t$  diagram for magnesium. 262°C.FIG. 9.  $E/t$  diagram for nickel. 270°C.

FIG. 10.  $E/t$  diagram for silver. 270°C.FIG. 11.  $E/t$  diagram for zinc. 278°C.Curve 1: pure molten  $\text{KHSO}_4$ Curve 2: molten  $\text{KHSO}_4$  with  $\text{ZnSO}_4$  (0.01 M).TABLE 1. GALVANIC SERIES IN MOLTEN  $\text{KHSO}_4$   
(TEMPERATURE RANGE: 260–280°C)  
REFERENCE ELECTRODE: Pt,  $\text{H}_2$  1 atm),  $\text{KHSO}_4(l)$ 

Metal	$E$ mV	$t$ min
Iron	$-205 \pm 10$	$\sim 10$
Nickel	$-330 \pm 25$	—
Cobalt	$-455 \pm 5$	$\sim 30$
Silver	$-460 \pm 10$	$\sim 5$
Copper	$-550 \pm 10$	$< 1$
Aluminium	$-630 \pm 20$	$\sim 60$
Cadmium	$-820 \pm 10$	$\sim 120$
Lead	$-830 \pm 5$	$\sim 60$
Magnesium	$-1210 \pm 5$	$\sim 30$
Zinc	$-1530 \pm 10$	$\sim 15$

steady potential is not easily attained before 2 h, although a minimum of  $-385 \pm 5$  mV is attained after 45 min; after 2 h it is  $-330 \pm 25$  mV. Dissolution in the melt occurred.

*Silver.* The final steady potential is reached in less than 5 min (Fig. 10). The addition of silver ion in the form of silver sulphate shows that, qualitatively, the potential decreases slightly as the silver-ion concentration increases. However, at the end of each run the metal was coated with silver crystals. The final potential observed is  $-460 \pm 10$  mV.

*Zinc.* (Fig. 11) Zinc is similar to copper in the rapidity of reaching a steady value. The potential depends on the concentration of zinc in the melt; it increases in the sense of the Nernst equation, when zinc sulphate is added. It moves to  $-1530$  mV and then increases very slowly, whether or not zinc ions are present in the melt.

A series to indicate the tendencies of these metals to form galvanic cells, and to predict the probable direction of the galvanic effects, is shown in Table 1; it is similar to the galvanic series in aqueous solutions.<sup>3,4</sup> The time required to reach a potential within the assigned range of reproducibility is stated. It is probable that no passivation effects were involved in the experiments, except for aluminium.

In the range investigated, any temperature effect of corrosion potentials was within the limits of experimental error.

Further study of the kinetics of corrosion processes involved in molten potassium bisulphate including the effect of oxygen is now in progress and will be reported in the near future.

*Acknowledgement*—This work was in part made possible through assistance from the Consejo Nacional de Investigaciones Científicas y Técnicas of Argentina.

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