

EQUILIBRIUM POTENTIAL DIFFERENCE OF Na/Na(Hg)
CONCENTRATION CELL AT LOW AMALGAM CONCENTRATIONS
IN THE MEDIUM OF VERY DRY PROPYLENE CARBONATE

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The equilibrium potential difference of the cell Na(s)|NaClO₄ (0.01M), PC|Na(Hg) in the medium of highly dried propylene carbonate (PC) was measured in the temperature range 15–90°C. The composition of the sodium amalgam was in the range 0.09–5.4 at.% Na (up to saturation at 25°C). The equilibrium potential difference of the cell with amalgam in the liquid state at the studied temperatures and concentrations can be expressed as $E_{\text{cell},T} = 0.90617 - 6.6477 \cdot 10^{-4}T + 5.56827 \cdot 10^{-7}T^2 - (2.3026RT/F) [\log x'_{\text{Na}} + (22.3918 - 2.17916 \cdot 10^{-2}T) x'_{\text{Na}}]$. From this the standard equilibrium potentials of the sodium amalgam electrode in aqueous medium and other thermodynamic quantities for this system in the given range of temperatures and concentrations were determined.

Diluted sodium amalgams are formed in large quantities as intermediate products in the electrolytic production of chlorine and sodium hydroxide by the amalgam method¹ and have found use as anodes in amalgam-oxygen fuel cells² as well as reductants in certain chemical syntheses³. The equilibrium potential belongs to fundamental thermodynamic characteristics of this system, whose knowledge in the corresponding range of temperatures and concentrations is indispensable for the calculation of equilibrium data for reactions in which the amalgam participates.

The equilibrium potentials of diluted sodium amalgams were treated in a number of publications, mostly dealing with the potential measurement of concentration cells in aqueous or non-aqueous media^{4–14}. Some other measurements were done with the use of solid electrolytes (sodium glass at 350–400°C, ref.¹⁵, or sodium β -alumina at 30 or 25°C, ref.^{16,17}). In spite of these many data among which there is a more or less satisfactory agreement there exist only at 25°C sufficient data enabling to derive a correlation between the equilibrium potential and concentration from zero up to saturation¹⁸; at this temperature, the saturated amalgam reportedly coexists with a solid intermetallic compound NaHg₄ (ref.¹⁹; a critical thermodynamic analysis of the phase diagram data for the Na–Hg system in the mentioned concentration range see ref.²⁰). According to recent data, a suitable nonaqueous solvent for the work with alkali metals and their amalgams is propylene carbonate^{21–23}, which gives with AlCl₃ and an alkali metal salt a solution enabling electrolytic deposition of alkali metals²⁴. In this medium were measured also potential differences of concentration cells of the type M(s)|M⁺X⁻(PC)|M(Hg), where X⁻ = AlCl₄⁻ or PF₆⁻, at 25–50°C (ref.²⁵). For the sodium amalgam, however, only two reliable values were reported at 25°C in the cited work and their connecting line did not correspond to

the concentration dependence derived from a critical survey of the published data¹⁸. A possible reason for this may be an insufficient drying of the propylene carbonate used.

Since we succeeded in elaborating a reliable method for the preparation of the NaClO₄-PC electrolyte with an unusually low water content, we have made use of it in the investigation of the cells Na(s)|NaClO₄(PC)|Na(Hg) in the range from very dilute to saturated amalgams in the temperature range 15–90°C; the aim was to obtain sufficiently reliable data for equilibrium potentials of the sodium amalgam in the given range of concentrations and temperatures of practical importance. The data of Mussini and coworkers²⁶ were measured only up to 70°C in aqueous medium where the amalgam is likely to decompose spontaneously. Such a decomposition is evidenced by a rather systematic decrease of the measured potentials²⁶ in very diluted solutions as compared with more concentrated NaCl (the values in 0.05 *m*-NaCl were about by 1–2 mV lower than in 1 *m*-NaCl, the most concentrated solution used). Also the amalgam concentration was rather low ($x'_{\text{Na}} < 0.01$) (ref.²⁶) as compared with saturated amalgam ($x'_{\text{Na, sat}} = 0.054$ at 25°C).

The results of the first part of our measurements of equilibrium potentials of concentration cells of the given type with sodium amalgams which are (except for the temperature of 15°C) liquid in the whole measured temperature range form the subject of this work.

EXPERIMENTAL

Apparatus and Chemicals

Sodium amalgam was prepared by dissolving sodium of reagent grade (Lachema, Brno) in redistilled mercury under vacuum, filtering through a glass capillary into an evacuated ampoule and then filled under vacuo into several dried ampoules 1 (Fig. 1). One or two of these stock ampoules with the amalgam were analysed to determine the sodium content. To prevent deposition of the solid phase in the most concentrated amalgam, its temperature was kept above 25°C.

A solution of 0.5M-NaClO₄ of reagent grade in propylene carbonate was prepared and dried in several stages by the molecular sieve Nalsit 4 under vacuum; in this way its water content was made lower than 15 ppm. The solution was then further dried by means of a film of sodium evaporated onto the walls of a glass bulb; the passivation of the sodium surface was prevented by periodical abrasion by means of sharp pieces of glass tubes with which the bulb was partially filled. (The details of the preparation of aprotic electrolytes were given elsewhere^{27,28}). The water content in the electrolyte was after this procedure lower than 3 ppm as determined by the Fischer method with increased sensitivity²⁹. This electrolyte was then diluted by dried propylene carbonate in a dried evacuated apparatus to a concentration of 0.01M. The solvent was prior to use dried by a long-term contact with an eutectic Na–K alloy, which was then separated *in vacuo* by filtration through a fritted glass disc and the propylene carbonate was vapour-transferred in a sealed evacuated glass apparatus into a condenser cooled with liquid nitrogen. An electrochemical analysis³⁰ revealed that the water content in the dried PC was lower than 10⁻² ppm. From the dilution ratio of 1 : 50 follows for the final solution of 0.01M-NaClO₄ in PC the water content

lower than 0.1 ppm. The stock amount of the electrolyte thus prepared was filled into evacuated ampoules 2 (Fig. 1) dried *in vacuo* at 300°C.

A part of the filling apparatus from the stopcock 12 to the hollow stopper 9 was dried by evacuating to $1.33 \cdot 10^{-2}$ Pa and periodical purging with dry helium (dried and deoxygenated at an overpressure of 10–15 MPa in a steel container in contact with a liquid eutectic Na–K alloy). Pieces of sodium 14 were evacuated in the space 13 through the stopcock 12 and melted; the melt was purified by filtering through slit 15 and heated in the compartment 17 to remove hydrogen dissolved in the metal. Afterwards it was transported by the action of dry helium through tube 16 into electrode compartment 19, where it solidified. The filling part of the apparatus was then sealed off under vacuum at 18. The contact with sodium was made by a Kovar wire 20 which reached into tube 21 filled with mercury, and by a further isolated lead to terminals of a measuring device.

The other part of the apparatus was also dried by evacuating and purging with helium through stopcock 7. By means of an electromagnet and a nickel piece 4 the tube 3 was then broken and the sodium amalgam of a known concentration flowed out from ampoule 1 through tube 5 into evacuated compartment 11. A contact between the amalgam and mercury in tube 8 was mediated by a Kovar wire 10. Ampoule 2 with the dry electrolyte was later opened in the same way and the electrolyte filled the space above the amalgam. By the end of tube 5 whose motion was enabled by a vacuum-tight joint (Sovirel, France) 6 with a silicon rubber gasket, the hollow stopper 9 was broken off so that the electrolyte was sucked into the evacuated space above the sodium electrode. The space above the electrolyte was then filled through stopcock 7 by dry helium at atmospheric pressure. The use of the described procedure ensures that the extremely low content of water and oxygen in the solutions is maintained during the measurement, as evidenced by the earlier work^{27–30}.

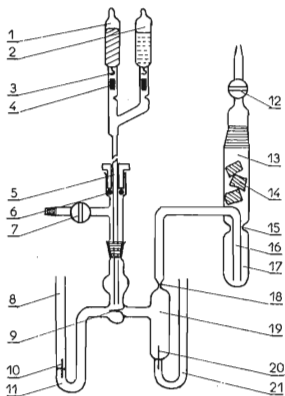


FIG. 1
Scheme of Apparatus for Preparation of Concentration Cells $\text{Na(s)}|\text{NaClO}_4(0.01\text{M})(\text{PC})|$
 $|\text{Na}(\text{Hg})$

Description given in the text.

Method of Measurement

The vessel with the concentration cell of a known composition prepared as indicated above was dipped into a tempered bath whose temperature was maintained at 15–40°C with an accuracy to $\pm 0.05^\circ\text{C}$ and at 65–90°C with an accuracy to $\pm 0.1^\circ\text{C}$. Immediately afterwards, the measurement of the equilibrium potential difference of the cell was begun by means of a digital voltmeter IDV 1200 (Aritma, Prague) enabling to read the voltage values with a sensitivity of 0.01 mV. The measured potential difference of the cell reached relatively rapidly a constant value, not later than after 10 min. If the potential changed during further 10 min at most by ± 0.1 mV, the measurement was finished, the vessel was transferred into another bath tempered to another temperature and the measurement continued analogously. At first the vessel was transferred into baths with gradually increasing temperatures and after attaining the highest temperature the whole procedure was repeated in the descending order. The differences between the steady potentials at the same temperature did not exceed ± 0.2 mV, while the whole series of measurements lasted for 3–4 h. This agreement can be considered as a proof of the reliability and stability of the measurement in the whole range of temperatures and concentrations and at the same time it follows that the measured values represent the equilibrium potentials of the cell under study. If the measurement was repeated with an amalgam of the same composition, the potential values differed by not more than 0.1 mV. The rate of attainment of the steady value of the potential difference was the higher the higher the temperature.

RESULTS AND DISCUSSION

The measured potentials of the cell $\text{Na(s)}|\text{NaClO}_4(0.01\text{M})|\text{Na(Hg)}$ are summarized in Table I (mean values at the given composition and temperature). The mole fraction of the total sodium in the amalgam was in the range $x'_{\text{Na}} = 0.0009 - 0.054$

TABLE I

Measured and Calculated Values of Equilibrium Differences Potential of the Concentration Cell $\text{Na(s)}|\text{NaClO}_4(0.01\text{M})|\text{PC}|\text{Na(Hg)}$

x'_{Na}	$E_{\text{cell}}, \text{K}$									
	288.15		298.15		315.15		338.15		363.15	
	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.
0.00092411	0.93348	0.93348	0.93625	0.93606	0.94030	0.94019	0.94750	0.94772	0.95570	0.95585
0.0026983	—	—	—	—	—	—	0.91530	0.91470	0.92075	0.92048
0.00843485	0.87160	0.87165	0.87210	0.87223	0.87320	0.87327	0.87520	0.87570	0.87858	0.87882
0.0282847	0.82335	0.82338	0.82235	0.82250	0.82130	0.82139	0.82060	0.82044	0.82048	0.82026
0.0420924	0.80095	0.80072	0.79945	0.79929	0.79736	0.79727	0.79490	0.79494	0.79330	0.79341
0.054000 ^a	0.79081 ^a	0.79100	0.78175	0.78175	0.79903	0.79903	0.77568	0.77569	0.77320	0.77321

^a At 288.15 K the Na amalgam of this composition is oversaturated, so the concentration of saturated amalgam $x'_{\text{Na}} = 0.0487$ (ref.⁴) was used in the correlation equation (2).

(up to saturated amalgam at 25°C), so that except for the most concentrated amalgam at 15°C the amalgams were liquid at all the experimental temperatures (15, 25, 40, 65, and 90°C).

After a longer time, especially at higher temperatures, some reaction taking place between the amalgam and PC in the measuring vessel was manifested by covering the amalgam surface with a thin film of insoluble reaction products²². The mentioned agreement between the potentials measured at both increasing and decreasing temperatures suggests, however, that the rate of this reaction was so small as to make the loss of sodium in the amalgam during the measurement negligibly small. The sodium electrode is during contact with PC covered with a carbonate film²², which is ionically conductive and hence does not prevent the establishment and measurement of the reversible potential.

The dependence of the measured potential difference E_{cell} on the amalgam concentration (expressed in mole fraction x'_{Na}) can be expressed in the form^{5,17,18}

$$E_{\text{cell},T} = E_{\text{cell},T}^0 - (2 \cdot 3026RT/F) (\log x'_{\text{Na}} + k_T x'_{\text{Na}}). \quad (1)$$

This equation can be rewritten in the form

$$\begin{aligned} E'_{\text{cell},T} &= E_{\text{cell},T} + (2 \cdot 3026RT/F) \log x'_{\text{Na}} = \\ &= E_{\text{cell},T}^0 - (2 \cdot 3026RT/F) k_T x'_{\text{Na}}, \end{aligned} \quad (2)$$

according to which a straight line should be obtained by plotting $E'_{\text{cell},T}$ against x'_{Na} . The slope of this dependence is $-2 \cdot 3026RTk_T/F$ and the section on the ordinate axis gives $E_{\text{cell},T}^0$. The values of $E_{\text{cell},T}^0$ and k_T were calculated by the least squares method. In this way we arrived at results given in Table II. The agreement of the measured values with the straight lines from the correlation (2) is very good in the whole studied concentration range, which at 15 and 25°C reaches from the diluted to saturated amalgams. Only the experimental point for the saturated amalgam at 15°C (Table I) deviates from the linear correlation since this amalgam contained a solid phase and hence did not contain the whole sodium in the liquid phase. In other cases, the very good agreement between the correlation equation and the measured data is demonstrated by comparison of calculated potential differences (with the use of $E_{\text{cell},T}^0$ and k_T from Table II) with the measured ones (Table I).

It follows from Table II that both quantities, $E_{\text{cell},T}^0$ and k_T , depend on the temperature. The former was expressed by a quadratic equation

$$E_{\text{cell},T}^0 = 0.90617 - 6.6477 \cdot 10^{-4}T + 5.56827 \cdot 10^{-7}T^2. \quad (3)$$

which holds with a mean relative error of $1.39 \cdot 10^{-3}\%$. The temperature dependence

of the coefficient k_T is linear:

$$k_T = 22.2918 - 2.17916 \cdot 10^{-2} T \quad (4)$$

with a mean relative deviation from experimental data (Table II) $7.32 \cdot 10^{-2}\%$. The accuracy of Eqs (3) and (4) is sufficient to express the equilibrium potential difference of the cell under study as a function of the amalgam concentration and temperature:

$$E_{\text{cell},T} = 0.90617 - 6.6477 \cdot 10^{-4} T + 5.56827 \cdot 10^{-7} T^2 - \\ - (2.3026RT/F) [\log x'_{\text{Na}} + (22.2918 - 2.17916 \cdot 10^{-2} T) x'_{\text{Na}}]. \quad (5)$$

The quantity $E_{\text{cell},T}^0$ denotes¹⁸ the standard potential difference of the cell formed by pure sodium and a hypothetical sodium amalgam of a mole fraction $x'_{\text{Na}} = 1$,

TABLE II

Thermodynamic Quantities Calculated from Measured Equilibrium Potential Differences of the Cell Na(s)|NaClO₄ (0.01M)(PC)|Na(Hg)

Line	Quantity	Temperature, K					Way of determ.
		288-15	298-15	313-15	338-15	363-15	
1	$E_{\text{cell}}^0, \text{V}$	0.76097	0.75746	0.75258	0.74506	0.73818	Eq. (2) and exp. d.
2		0.76085	0.75746	0.75260	0.74504	0.73819	Eq. (3)
3	k	16.1173	15.8714	15.5903	15.0244	14.4729	Eq. (2) and exp. d.
4		16.1126	15.8947	15.5678	15.0230	14.4582	Eq. (4)
5		16.415	16.335	16.216	16.015	15.815	after Mussini and coworkers ²⁶
6	$-E_{\text{Na(s)/Na}^+(\text{aq})}^0, \text{V}$	2.70702	2.71414	2.72507	2.74312	2.76117	using (dE^0/dT) (ref. ³¹)
7		2.70671	2.71424	2.72566	2.74500	2.76468	Eq. (9)
8	$-E_{\text{Na(Hg)/Na}^+(\text{aq})}^0, \text{V}$	1.94617	1.95678	1.97247	1.99807	2.02298	from data in lines 2 and 6
9		1.94586	1.95678	1.97306	1.99996	2.02649	from data in lines 2 and 7
10		1.94758	1.95909	1.97604	2.00343	2.02975	Eq. (8), see ref. ²⁶
11	$\log K$	13.30771	12.80418	12.11254	11.10447	10.24485	from data in line 2
12		13.30277	12.80418	12.11818	11.10917	10.23908	Eq. (13)
13	ΔS^0 for NaHg _m J/mol K	5.640	5.613	5.573	5.506	5.439	from $\partial E^0/\partial T$

whose state was derived by extrapolation from the reference state of infinitely diluted solution where the activity coefficient of sodium was set equal to 1. By combining this quantity with the standard potential of pure metallic sodium in aqueous medium $E_{\text{Na(s)/Na}^+(\text{aq})}^0$ it is possible to obtain the standard potential of the sodium amalgam in aqueous medium at the corresponding temperature:

$$E_{\text{Na(Hg)/Na}^+(\text{aq})}^0 = E_{\text{Na(s)/Na}^+(\text{aq})}^0 + E_{\text{cell,T}}^0 \quad (6)$$

If we take the most exact value¹⁸ $E_{\text{Na(s)/Na}^+(\text{aq})}^0 = -2.71424$ V at 25°C with the temperature coefficient given by de Béthun³¹ assuming its validity in the whole range of temperatures, we arrive at results given in Table II. From these we obtain the following temperature dependence:

$$E_{\text{Na(Hg)/Na}^+(\text{aq})}^0 = -1.59289 - 1.38624 \cdot 10^{-3}T + 5.55973 \cdot 10^{-7}T^2 \quad (7)$$

The mean relative deviation of the data according to Eq. (6) from those according to Table II at the given temperatures is only $6.63 \cdot 10^{-5}\%$. Mussini and coworkers²⁶ obtained for the same quantity from their measurements in aqueous NaCl solutions for a much narrower range of amalgam concentrations an analogous dependence with somewhat different constants:

$$E_{\text{Na(Hg)/Na}^+(\text{aq})}^0 = -1.54188 - 1.65575 \cdot 10^{-3}T + 8.6000 \cdot 10^{-7}T^2 \quad (8)$$

The difference between the standard potentials calculated from Eqs (7) and (8) increases with the temperature from 15 to 90°C. For this reason, we calculated the standard potential of the sodium electrode also by another method, based on recently tabulated thermodynamic data for Na and Na⁺ ions in the standard state in aqueous medium³² together with molar heat capacities, C_p^0 . On the assumption that the values of C_p^0 at 25°C can be used with a sufficient accuracy for the whole temperature interval under study, we have the following equation:

$$-FE_T^0 = \Delta H_{298.15}^0 - T\Delta S_{298.15}^0 - T\Delta C_p^0 \left(\ln \frac{T}{298.15} + \frac{298.15}{T} - 1 \right), \quad (9)$$

where the thermodynamic data for the reaction $\text{Na}^+(\text{aq}) + e = \text{Na(s)}$ are: $\Delta H_{298.15}^0 = 240120$ J/mol, $\Delta S_{298.15}^0 = -73.015$ J/mol K, and $\Delta C_{p,298.15}^0 = -18.2$ J/mol K.* The values of $E_{\text{Na(s)/Na}^+(\text{aq})}^0$ calculated in this way are also given in Table II. The values of $E_{\text{Na(Hg)/Na}^+(\text{aq})}^0$ calculated on their basis are not so largely different from the cor-

* The original tabulated data in cal were recalculated to J units with the use of the relation 1 cal (thermochem.) = 4.184 J.

responding data of Mussini and coworkers²⁶. Hence it can be concluded that the temperature coefficient of the sodium electrode given by de Béthune³¹ is not applicable for the whole temperature range. Nevertheless, both the latter series' of the standard potentials of the Na(Hg) electrode show especially at higher temperatures differences which are too large for exact calculations to follow. A possible reason for this may be both the experimental errors in the measurement of the temperature dependence and an insufficient accuracy of the correlation equation used in the whole temperature range.

The dependence of the standard potential of the Na(Hg) electrode on the temperature according to the latter calculation based on Eq. (9) can be expressed by an equation similar to (7) and (8):

$$E_{\text{Na(Hg)/Na}^+(\text{aq})}^0 = 1.60844 - 1.24707 \cdot 10^{-3}T + 2.64004 \cdot 10^{-7}T^2, \quad (10)$$

which fits the basic data with a mean relative error of $1.7 \cdot 10^{-4}\%$. Similarly, the latter calculated values of $E_{\text{Na(s)/Na}^+(\text{aq})}^0$ can be expressed by the temperature function

$$E_{\text{Na(s)/Na}^+(\text{aq})}^0 = -2.51410 - 5.85388 \cdot 10^{-4}T - 2.88009 \cdot 10^{-7}T^2, \quad (11)$$

which fits the basic data with a mean relative deviation of $6.84 \cdot 10^{-5}\%$.

By differentiating the dependence of the standard potential difference of the cell Na(s)/Na⁺X⁻/Na(Hg) (Eq. (3)) on the temperature, it is possible to calculate the standard entropy difference of the cell reaction, $\Delta S_T^0 = nF(\partial E^0/\partial T)$ (Table II).

It follows from the preceding work³³ that in the case where the amalgam contains intermetallic compounds the quantity $E_{\text{cell},T}^0$ is related to the equilibrium constant K_T of the intermetallic compound MHg_m according to the equation

$$nFE_{\text{cell},T}^0 = RT \ln K_T. \quad (12)$$

From this value, however, the stoichiometric coefficient m of the compound MHg_m cannot be derived. The decadic logarithms of the equilibrium constant K_T at different temperatures determined in this way are given also in Table II. Their temperature dependence is given by the van't Hoff equation as

$$\log K_T = -1.52971_2 + 4273.84/T, \quad (13)$$

which fits the given data with a mean relative deviation of $3.84 \cdot 10^{-2}\%$. From the second term on the right-hand side it is possible to calculate the standard enthalpy change corresponding to the formation of the intermetallic compound in the standard state, $\Delta H^0 = -35534 \text{ J/mol}$, which is practically independent of the temperature in the range considered. From this finding it can be concluded that the composition

of the intermetallic compound in diluted sodium amalgams (where also a unique concentration dependence in the whole concentration range is observed, *cf.* Fig. 1) remains unaltered in the whole range of temperatures and concentrations.

The comparison of the concentration dependence of the equilibrium potentials E_{cell} measured in this work with the results of other authors in the whole studied concentration range is possible only for the temperature of 25°C on the basis of the published review¹⁸. At other temperatures the concentration ranges measured by other authors are too narrow. According to our work, $E_{\text{cell}}^0 = 0.75746 \text{ V}$ (25°C); an analogous treatment of data obtained by other authors in nonaqueous medium¹⁸ leads to the value $E_{\text{cell}}^0 = 0.75840 \text{ V}$, the difference being 0.94 mV. Similarly the k value in Eq. (1), according to our measurements equal to 15.871 at 25°C (or after the temperature correlation according to Eq. (4) 15.895), is according to the evaluation of other data¹⁸ equal to 16.393 or 16.40.

After plotting our measured data together with those of other authors according to the form of Eq. (2) it turned out, however, that two measurements of Bent and Swift⁴ for two most concentrated amalgams deviate markedly from the rather smooth curve. From an evaluation of all data available from our and other work excluding the two mentioned deviating values we obtained the following values of the characteristic constants of Eq. (1) at 25°C: $E_{\text{cell}}^0 = 0.75800 \pm 1.38 \cdot 10^{-4} \text{ V}$, $k = 16.000 \pm 0.090$. An analogous evaluation of all the data available (including the deviating ones) gave $E_{\text{cell}}^0 = 0.75718 \pm 2.12 \cdot 10^{-4} \text{ V}$, $k = 16.252 \pm 0.0123$. The deviating two values of Bent and Swift⁴ exert a rather large influence on the final constants E_{cell}^0 and k . Therefore, the mean values $E_{\text{cell}}^0 = 0.7580 \text{ V}$ and $k = 16.00$ are according to our opinion preferable. If we compare our measured values of these quantities with the former ones we find a very good agreement. Since the reliability of our measurements was at all temperatures the same (as evidenced by the reproducibility of the measurements during decreasing and increasing temperature), the measured data at other temperatures can also be considered as reliable. This applies mainly for the measured equilibrium potentials of the concentration cells, the resulting characteristic constants $E_{\text{cell},T}^0$ and k_T and the equilibrium constants K_T of formation of intermetallic compound NaHg_m . The derived quantity $E_{\text{Na(Hg)}/\text{Na}^+(\text{aq})}^0$ must be judged with care since the accuracy with which the standard potential of the sodium electrode at temperatures different from 25°C was calculated is not known (*cf.* its values in Table II obtained according to Eq. (9) and from the temperature coefficient of the sodium electrode according to de Béthune³¹). The ΔH^0 value for the amalgamation reaction following from the temperature dependence of the equilibrium constant of the formation of NaHg_m , Eq. (13), is independent of the temperature, an evidence that the assumption $\Delta C_p^0 = \text{const.}$ involved in Eq. (9) is justified (in the opposite case the value of ΔH^0 would depend on the temperature).

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