THERMODYNAMIC RELATIONS FOR AMALGAM DECOMPOSERS*

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Equations are derived to calculate the electromotive force of the cell $NaHg_x|NaOH, H_2O|H_2|Pt$ at $25-100°C$, sodium concentration $0-0.5$ wt.% and concentration of soda lye $0-50$ wt.%. Expressions for the reaction enthalpy of sodium amalgam decomposition, activity of water in the soda lye and electromotive force of the cell $Pt|H_2|NaOH, H_2O|HgO|Hg$ in the given range of temperatures and concentrations are also presented. Calculated values of the thermodynamic functions are tabulated and compared with literature data.

In the industrial production of chlorine and soda lye in electrolysers with a mercury cathode, gaseous chlorine is evolved at the anode and sodium amalgam in the cathode. The amalgam is decomposed with water in a decomposer filled with a graphite bed to give soda lye:

$$NaHg_x + H_2O = NaOH + \tfrac{1}{2}H_2 + x\,Hg. \qquad (A)$$
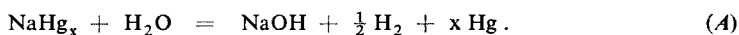
This reaction is electrochemical in character; the amalgam and graphite form a short-circuited galvanic cell of the type

$$NaHg_x \,|\, NaOH,\, H_2O \,|\, H_2 \,|\, C. \qquad (B)$$
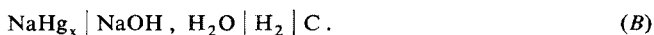
With respect to the increasing performance of modern amalgam electrolysers, considerable attention has been paid nowadays to a rational design of decomposers. Thermodynamic relations derived in this work will be used later in evaluating the kinetics of the decomposition process and in engineering studies of the decomposers.

The electromotive force, E, of the cell (B), which is the driving force of the reaction (A), is given by the Nernst equation:

$$E = -\varepsilon^0_{Na} + \varepsilon^0_{H_2/OH^-} - (RT/F)\ln\left(m^2\gamma^2_{NaOH\pm}p^{0.5}_{H_2}/a_{H_2O}a_{Na}\right). \qquad (1)$$

Sufficiently reliable data to calculate the value of E from Eq. (1) are available only for lower temperatures, mainly 25°C. If the value of E for another temperature is
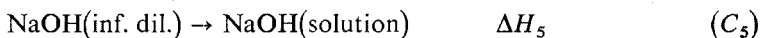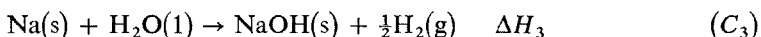
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needed, use is made of the Gibbs–Helmholtz equation

$$\partial(E/T)/\partial T = \Delta H_r/FT^2 , \tag{2}$$

which is integrated and the integration constant determined from the value of E at 25°C. The electromotive force, E, is a basic thermodynamic quantity used in further calculations; equations for the other quantities are based on equations for E. We shall find first an equation for the dependence of the reaction enthalpy, ΔH_r, on concentration and temperature, which is needed for integration of Eq. (2).

Reaction Enthalpy of Amalgam Decomposition

Reaction enthalpy at 25°C. Reaction (A) is thought to be composed of a sequence of steps, the reaction enthalpies of which are denoted as ΔH_1 through ΔH_5:

$$H_2O(\text{solution}) \rightarrow H_2O(1) \qquad \Delta H_1 \qquad (C_1)$$

$$Na(\text{amalgam}) \rightarrow Na(s) \qquad \Delta H_2 \qquad (C_2)$$

$$Na(s) + H_2O(1) \rightarrow NaOH(s) + \tfrac{1}{2}H_2(g) \quad \Delta H_3 \qquad (C_3)$$

$$NaOH(s) \rightarrow NaOH(\text{inf. dil.}) \qquad \Delta H_4 \qquad (C_4)$$

$$NaOH(\text{inf. dil.}) \rightarrow NaOH(\text{solution}) \qquad \Delta H_5 \qquad (C_5)$$

Partial relative molar enthalpy of water and NaOH *at 25°C.* The reaction enthalpies $-\Delta H_1$ and ΔH_5 are equal to partial relative molar enthalpies $\bar{L}_{H_2O}$ and $\bar{L}_{NaOH}$ defined as

$$\bar{L}_{H_2O} = \bar{H}_{H_2O} - \bar{H}^0_{H_2O} , \qquad \bar{L}_{NaOH} = \bar{H}_{NaOH} - \bar{H}^0_{NaOH} . \tag{3),(4}$$

Bertetti and McCabe[1] presented the dependence of the total relative enthalpy of a mass unit of sodium hydroxide solution (referred to infinite dilution), ΔH_{BC}, on concentration at 20°C. From these data we can calculate the total relative enthalpy, ΔH_L^{rel} (referred to infinite dilution) at 20°C for 1 mol of the solution of a given composition:

$$\Delta H^{rel}_{L,293} = (5/9) \Delta H_{BC}(mM_{NaOH} + 1000)/(m + 55.506) , \tag{5}$$

where 55.506 is the value of $1000/M_{H_2O}$. The value of ΔH_L^{rel} at 25°C is obtained from that at 20°C by means of the equation

$$\partial \Delta H^{rel}_L/\partial T = C_{p,L} - C^0_{p,L} . \tag{6}$$

The heat capacities of sodium hydroxide solutions at $15.5 - 93.3°C$ and for $0 - 52$ wt.%

NaOH were determined by the same authors[2] whose data were approximated for our purpose by the formula

$$C_{p,L} = \sum_{i=0}^{5} \sum_{j=0}^{4} z_{ij} m^i T^j .$$ (7)

The constants z_{ij} are given in Table I. The average deviation of this correlation with respect to the original data[2] is 0.09%. The high accuracy of this complicated interpolation formula is necessary for further calculations.

The molar heat capacity $C_{p,L}^0$ is given as

$$C_{p,L}^0 = \left(55.506 \bar{C}_{p,H_2O}^0 + m \bar{C}_{p,NaOH}^0\right)/(m + 55.506) .$$ (8)

TABLE I

Constants $z_{i,j}$ and a_i for Equations (7) and (9)

j	$z_{0,j}$	$z_{1,j}$	$z_{2,j}$
0	$1.6611716 . 10^1$	$-1.7640072 . 10^1$	3.2720989
1	$1.4422309 . 10^{-2}$	$1.2403064 . 10^{-1}$	$-2.3907983 . 10^{-2}$
2	$-5.5790899 . 10^{-5}$	$-2.2534877 . 10^{-4}$	$4.5883197 . 10^{-5}$
3	$6.7517106 . 10^{-8}$	$-1.3466098 . 10^{-7}$	$2.6362737 . 10^{-8}$
4	$2.1415684 . 10^{-11}$	$4.8162039 . 10^{-10}$	$-1.0418906 . 10^{-10}$

j	$z_{3,j}$	$z_{4,j}$	$z_{5,j}$
0	$-2.6829375 . 10^{-1}$	$1.0167708 . 10^{-2}$	$-1.4417268 . 10^{-4}$
1	$2.0031959 . 10^{-3}$	$-7.6691165 . 10^{-5}$	$1.1091959 . 10^{-6}$
2	$-3.9529814 . 10^{-6}$	$1.5519122 . 10^{-7}$	$-2.4049632 . 10^{-9}$
3	$-2.0805888 . 10^{-9}$	$6.4168259 . 10^{-11}$	$-2.4012589 . 10^{-13}$
4	$8.9403036 . 10^{-12}$	$-3.2661056 . 10^{-13}$	$3.9264474 . 10^{-15}$

i	$a_i(0.1 \leqq m \leqq 6)$	$a_i(6 < m \leqq 23)$
0	$-2.48275 . 10^{-2}$	$-3.73516 . 10^1$
1	3.13780	$2.53337 . 10^1$
2	-1.95552	-7.58072
3	$4.53531 . 10^{-2}$	1.01168
4	$9.06609 . 10^{-2}$	$-3.81358 . 10^{-2}$
5	$-7.94703 . 10^{-3}$	$4.86980 . 10^{-4}$

The temperature dependence of $\bar{C}^0_{p,H_2O}$ was on the basis of tabulated data[3] for 20 to 100°C expressed as $\bar{C}^0_{p,H_2O} = 22\cdot161 - 0\cdot027455T + 4\cdot4987 \cdot 10^{-5}T^2$ with an error smaller than 0·02 cal/mol K. For $\bar{C}^0_{p,NaOH}$ it is possible to derive from the published data[4] the equation $\bar{C}^0_{p,NaOH} = -114\cdot39 + 0\cdot28571T$ valid for $18-25°C$.

After substituting for the heat capacities, Eq. (6) was integrated from 293·15 to 298·15K for individual values of $\Delta H^{rel}_{L,293}$ calculated from Eq. (5) with the use of the original data[1]. The obtained dependence of $\Delta H^{rel}_{L,298}$ on concentration of the solution can be approximated with an error smaller than 0·1 cal/mol by the power series

$$\Delta H^{rel}_{L,298} = \sum_{i=0}^{5} a_i m^i , \tag{9}$$

where the constants a_i are given in Table I. From the known concentration dependence of $\Delta H^{rel}_{L,298}$ we obtain with the aid of the Gibbs–Duhem equation the result

$$\bar{L}_{H_2O,298} = \Delta H^{rel}_{L,298} - m(m/55\cdot506 + 1)\, \partial\Delta H^{rel}_{L,298}/\partial m , \tag{10}$$

$$\bar{L}_{NaOH,298} = \Delta H^{rel}_{L,298} + (m + 55\cdot506)\, \partial\Delta H^{rel}_{L,298}/\partial m . \tag{11}$$

Differential enthalpy of solution for sodium in amalgam at 25°C. The reaction enthalpy ΔH_2 is equal to the differential enthalpy of solution for sodium in the amalgam, $\bar{L}_{Na}$, taken with opposite sign. The dependence of $\bar{L}_{Na}$ on mole fraction of sodium, X_{Na}, at 25°C is tabulated in ref.[5] and can be expressed as

$$\bar{L}_{Na,298} = -19956 + 4643X_{Na} \tag{12}$$

with an error less than 0·02%. This relation can be checked with the use of the temperature dependence of the sodium activity in the amalgam:

$$\partial \log a_{Na}/\partial T = -\bar{L}_{Na}/2\cdot30259RT^2 . \tag{13}$$

The activity of sodium in the amalgam at $5-25°C$ was expressed by Bent and Swift[6] for $X_{Na} \leqq 0\cdot049$ as

$$\log(a_{Na}/X_{Na}) = -8387\cdot6/T^{1\cdot138} + (338\cdot2/T^{0\cdot54})\,X_{Na} + 7X_{Na}^2 . \tag{14}$$

Newer data about equilibrium potentials of the amalgam electrode in sodium chloride solutions and activity of sodium in diluted amalgams ($X_{Na} \leqq 0\cdot01$) were presented by Mussini and coworkers[7], however they differ according to Balej[30] from other literature data by $2-3$ mV at 25°C probably owing to a decomposition of the amalgam in contact with the aqueous electrolyte. To check Eq. (12) and to calculate a_{Na} at

25°C, we therefore use Eq. *(14)*. By combining Eq. *(13)* with *(14)* and setting $T = 298 \cdot 15K$ we obtain

$$\bar{L}_{Na,298} = -19896 + 11488X_{Na} \,. \tag{15}$$

The values of $\bar{L}_{Na,298}$ calculated from Eq. *(15)* differ from those from *(12)* by not more than $2 \cdot 1\%$ (for $X_{Na} = 0 \cdot 05$). We shall use further Eq. *(12)* for the calculation of $\bar{L}_{Na,298}$.

Reaction enthalpy of reaction (C_3) *and differential enthalpy of solution of* NaOH *at 25°C.* The change of enthalpy ΔH_3 for reaction (C_3) at 25°C can be calculated from the known heats of formation[8] of NaOH and H_2O: $\Delta H_3 = \Delta H^f_{NaOH,298} - \Delta H^f_{H_2O,298} = -101990 + 68317 = -33673$ cal/mol. The quantity ΔH_4 is the differential enthalpy of solution for 1 mol NaOH(s) at infinite dilution and is equal to -10179 cal/mol at 18°C (ref.[9]). Its value at 25°C is obtained with the use of the equation $\partial \Delta H_4 / \partial T = \bar{C}^0_{p,NaOH} - C^s_{p,NaOH}$. A formula for the molar heat capacity of NaOH at infinite dilution, $\bar{C}^0_{p,NaOH}$, was given in connection with Eq. *(8)*. The molar heat capacity of solid NaOH is given as[10] $C^s_{p,NaOH} = 4 \cdot 196 \,.\, 10^{-3}T + 12 \cdot 966$. By integration we obtain $\Delta H_4 \,(25°C) = -10490$ cal/mol.

The value of the sum $\Delta H_3 + \Delta H_4$ can be verified with the use of the temperature dependence of the standard electromotive force $E^0 = -\varepsilon^0_{Na} + \varepsilon^0_{H_2/OH^-}$. From Eq. *(2)* we obtain the standard reaction enthalpy, ΔH^0_r, which is with respect to the choice of the standard states equal to $\Delta H_3 + \Delta H_4$: $\Delta H^0_r = F(T \partial E^0 / \partial T - E^0)$. With the use of Eqs *(26)* and *(27)* for the standard potentials we obtain $\Delta H^0_r = -43922$ cal/mol, which differs from the sum $\Delta H_3 + \Delta H_4$ by 241 cal/mol, *i.e.* $0 \cdot 55\%$.

Final equation for reaction enthalpy ΔH_r *at 25°C.* This quantity for the decomposition reaction (A) is equal to the sum of ΔH_1 through ΔH_5:

$$\Delta H_{r,298} = -\bar{L}_{H_2O,298} + 19956 - 4643X_{Na} - 33673 - 10490 + \bar{L}_{NaOH,298} \,. \tag{16}$$

This equation can be rearranged with the use of Eq. *(9)* and

$$\bar{L}_{NaOH} - \bar{L}_{H_2O} = f_m \, \partial \Delta H^{rel}_L / \partial m \,, \tag{17}$$

where

$$f_m = (m + 55 \cdot 506)^2 / 55 \cdot 506 \tag{18}$$

so that the result is

$$\Delta H_{r,298} = -24207 - 4643X_{Na} + f_m \sum_{i=0}^{5} i a_i m^{i-1} \,. \tag{19}$$

Temperature dependence of reaction enthalpy. According to the Kirchhoff equation we have

$$\partial \Delta H_r / \partial T = \tfrac{1}{2} C_{p,H_2} + \bar{C}_{p,NaOH} - \bar{C}_{p,H_2O} - \bar{C}_{p,Na} . \tag{20}$$

The molar heat capacity of gaseous hydrogen is given by [11] $C_{p,H_2} = 6.6528 + 6.894$. $. 10^{-4} T$. The difference $\bar{C}_{p,NaOH} - \bar{C}_{p,H_2O}$ can be expressed by an equation similar to (17):

$$\bar{C}_{p,NaOH} - \bar{C}_{p,H_2O} = f_m \, \partial C_{p,L} / \partial m = f_m \sum_{i=0}^{5} \sum_{j=0}^{4} i z_{ij} m^{i-1} T^j . \tag{21}$$

The partial molar heat capacity of sodium in the amalgam, $\bar{C}_{p,Na}$, is calculated from the data of Balej and Vondrák[12] who expressed the specific heat capacity of the amalgam as $c_{p,am} = c_{p,Hg} + 2.386 . 10^{-3} N_{Na}$ at $20-50°C$ for $N_{Na} \leqq 0.52$ wt.%. (The numerical factor was given erroneously[12] as $2.386 . 10^{-4}$ owing to a printing error.) The heat capacity of 1 mol of the amalgam (corresponding to $X_{Na} M_{Na} + (1 - X_{Na})$. $. M_{Hg}$ in grams) is

$$C_{p,am} = c_{p,Hg}[X_{Na} M_{Na} + (1 - X_{Na}) M_{Hg}] + 0.2386 X_{Na} M_{Na} . \tag{22}$$

The partial molar heat capacity of sodium in the amalgam is

$$\bar{C}_{p,Na} = C_{p,am} + (1 - X_{Na}) \, \partial C_{p,am} / \partial X_{Na} = M_{Na}(c_{p,Hg} + 0.2386) . \tag{23}$$

We use the dependence of $c_{p,Hg}$ on temperature in the range $25-100°C$: $c_{p,Hg} =$ $= 0.034908 - 5.736 . 10^{-6} T$ as obtained from ref.[13]; then

$$\bar{C}_{p,Na} = 6.2879 - 1.3187 . 10^{-4} T . \tag{24}$$

We introduce the expressions for the heat capacities into Eq. (20) and after integration

TABLE II
Constants b_i and c_i for Equations (28) and (29)

i	$b_i (m \leqq 2)$	$b_i (2 < m \leqq 12)$	$b_i (12 < m \leqq 29)$	$c_i (0.1 \leqq m \leqq 29)$
0	$-9.69335 . 10^{-2}$	$-1.89355 . 10^{-1}$	-1.52142	$-1.45952 . 10^{-2}$
1	$-2.46046 . 10^{-1}$	$-2.25790 . 10^{-3}$	$2.80645 . 10^{-1}$	$-5.42148 . 10^{-5}$
2	$3.00042 . 10^{-1}$	$1.15270 . 10^{-2}$	$-9.22988 . 10^{-3}$	$-3.04734 . 10^{-4}$
3	$-1.54717 . 10^{-1}$	$-4.83240 . 10^{-4}$	$1.13921 . 10^{-4}$	$1.68615 . 10^{-5}$
4	$2.98788 . 10^{-2}$	$5.15369 . 10^{-6}$	$-1.50283 . 10^{-7}$	$-2.55787 . 10^{-7}$

from 298·15K to T obtain the final expression for ΔH_r as a function of temperature and concentrations of the soda lye and amalgam:

$$\Delta H_r = -23345 - 4643X_{Na} + f_m \sum_{i=0}^{5} ia_i m^{i-1} - 2·9615T + 2·3829 \cdot 10^{-4}T^2 +$$

$$+ f_m \sum_{i=0}^{5} \sum_{j=0}^{4} iz_{ij}m^{i-1}(T^{j+1} - 298·15^{j+1})/(j+1). \tag{25}$$

Electromotive Force of the Amalgam–Hydrogen Cell

Standard potentials. The standard potentials of the sodium and alkaline hydrogen electrodes are given by[14]

$$\varepsilon_{Na}^0 = -2·714 - 7·72 \cdot 10^{-4}(t - 25), \tag{26}$$

$$\varepsilon_{H_2/OH^-}^0 = -0·82806 - 8·342 \cdot 10^{-4}(t - 25) - 3·636 \cdot 10^{-6}(t - 25)^2. \tag{27}$$

The error in the determination of ε_{Na}^0 at 25°C was estimated[15] as $\pm 0·5$ mV. The standard potential ε_{H_2/OH^-}^0 can be checked by the equation $\varepsilon_{H_2/OH^-}^0 = (RT/F) \ln K_{H_2O} = -0·82798$ V at 25°C (with $\log K_{H_2O} = -13·9965$ at 25°C according to ref.[16]), while Eq. (27) gives $-0·82806$ V; the difference is only 0·08 mV.

Activities and activity coefficients of reaction components at 25°C. Mean molar activity coefficients, $\gamma_{NaOH\pm}$, and osmotic coefficients ϕ at 25°C for sodium hydroxide solutions in the range from 0·1 to 29 m are given by Robinson and Stokes[17]. (The osmotic coefficient ϕ and the activity of water a_{H_2O} at 25°C fulfil the relation[18] $\log a_{H_2O} = -0·015648 \, m\phi$.) Most data of ref.[17] (for $2 \leq m \leq 29$) were obtained by isopiestic measurements[19]. The values of $\gamma_{NaOH\pm}$ and a_{H_2O} for $0·1-17$ m NaOH at $0-70$°C were also measured potentiometrically by Åkerlöf and Kegeles[20]; their values of $\gamma_{NaOH\pm}$ at 25°C are on the average by 3% higher than those of ref.[17]. The authors presented empirical formulas for the dependence of the activity coefficient on temperature and concentration of NaOH, however these do not permit extrapolation to $m > 17$ (*e.g.*, the extrapolated value of $\gamma_{NaOH\pm}$ for $m = 25$ at 25°C would be 67·2 in disagreement with the measured value[17] 28·0). In further calculations, we shall rely upon the data of ref.[17] expressed by the following interpolation formulas:

$$\log \gamma_{NaOH\pm,298} = \sum_{i=0}^{4} b_i m^i, \tag{28}$$

$$\log a_{H_2O,298} = \sum_{i=0}^{4} c_i m^{i+1}. \tag{29}$$

The constants b_i and c_i are given in Table II. Eq. (28) agrees with the original data to within ± 0.003, ± 0.0023 and ± 0.001 for $0.1 \leqq m \leqq 2$, $2 < m \leqq 12$ and $12 < < m \leqq 29$, respectively; similarly the largest error of Eq. (29) is 0.0064 for $0.1 \leqq m \leqq \leqq 29$. The activity of sodium in the amalgam at 25°C will be calculated from Eq. (14).

Final equation for the electromotive force of the amalgam–hydrogen cell. The value of E at E_{298}, is given by Eq. (1), where the standard potentials are expressed from (26) and (27) and the activities and activity coefficients from (14), (28) and (29). The partial pressure of hydrogen, p_{H_2}, is calculated from Eq. (31) at the temperature of interest. The value of E at different temperatures is obtained by integration of Eq. (2) on using (25) for ΔH_r. The result is

$$
\begin{aligned}
E = {} & E_{298}T/298.15 + (T/F)\{(23345 + 6434X_{Na} - f_m \sum_{i=0}^{5} ia_i m^{i-1})/T - \\
& - 2.9615 \ln T + 2.3829 \cdot 10^{-4}T + f_m \sum_{i=0}^{5} im^{i-1}[z_{i0}(\ln T + 298.15/T) + \\
& + \sum_{j=1}^{4} z_{ij}(T^j/j + 298.15^{j+1}/T)/(j+1)]\}_{298.15}^{T} \cdot
\end{aligned}
\tag{30}
$$

The partial pressure of hydrogen is calculated under the assumption that only hydrogen and water vapour are present in the gaseous phase:

$$
p_{H_2} = p_T - p_{H_2O} \cdot
\tag{31}
$$

Here p_T denotes total pressure and p_{H_2O} equilibrium pressure of water vapour above the soda lye at the temperature considered. It is obvious that close to the boiling point of the solution $p_{H_2} \ll p_T$ so that the value of E increases considerably as compared with the case $p_{H_2} \sim p_T$. For example, for 5% NaOH, 100°C and $p_T = = 1$ atm we have $p_{H_2O} = 0.955$ atm, $p_{H_2} = 0.045$ atm and the value of E differs by 50 mV from that at $p_{H_2} = 1$ atm.

Activity of Water in the Soda Lye and Water Vapour Tension above the Solution

The activity of water in the soda lye as a function of temperature can be calculated by integrating the equations

$$
\partial \log a_{H_2O}/\partial T = -\bar{L}_{H_2O}/2.30259RT^2 ,
\tag{32}
$$

$$
\delta \bar{L}_{H_2O}/\delta T = \bar{C}_{p,H_2O} - \bar{C}_{p,H_2O}^0 \cdot
\tag{33}
$$

The integration constants are found from known values of a_{H_2O} and $\bar{L}_{H_2O}$ at 25°C,

Eqs (29) and (10). Furthermore

$$\bar{C}_{p,H_2O} = C_{p,L} - m(m/55\cdot506 + 1)\,\partial C_{p,L}/\partial m\,. \tag{34}$$

After integrating Eqs (32) and (33) we obtain

$$\log a_{H_2O} = \log a_{H_2O,298} + (2\cdot30259R)^{-1}\,\{(\bar{L}_{H_2O,\;98} + 5784\cdot6)/T + 22\cdot161\ln T -$$

$$- 1\cdot3728\,.\,10^{-2}T + 7\cdot50\,.\,10^{-6}T^2 - \sum_{i=0}^{5}[1 - i(m/55\cdot506 + 1)]\,m^i\,.$$

$$.\,[z_{i0}(\ln T + 298\cdot15/T) + \sum_{j=1}^{4} z_{ij}(T^j/j + 298\cdot15^{j+1}/T)/(j + 1)]\}_{298.15}^{T} \tag{35}$$

The equilibrium tension of water vapour above the solution of NaOH is $p_{H_2O} = p_{H_2O}a_{H_2O}$ (for $p_{H_2O} \leqq 1$ atm the fugacity of water vapour can be replaced by its partial pressure with a sufficient accuracy[26]). The equilibrium tension of water vapour above pure water can be calculated from the equation[27]

$$\log p^0_{H_2O} = (5\cdot13621T - 1916\cdot73)/(T - 42\cdot150)\,. \tag{36}$$

Electromotive Force of the Cell $Pt|H_2|NaOH,H_2O|HgO|Hg$

In measuring the overvoltage of hydrogen on graphite, we used[31] a $Hg|HgO$ reference electrode. To evaluate the experimental data, we need therefore to know the electromotive force, E', of the cell

$$Pt|H_2|NaOH,H_2O|HgO|Hg \tag{D}$$
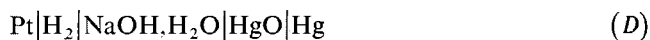
in dependence on concentration of NaOH and temperature. We proceed similarly as in calculating the electromotive force of the amalgam–hydrogen cell. The reaction in the cell (D) is $H_2 + HgO = H_2O + Hg$; according to the Nernst equation we have

$$E' = -\varepsilon^0_{H_2/OH^-} + \varepsilon^0_{Hg/HgO} - (RT/2F)\ln(a_{H_2O}/p_{H_2})\,. \tag{37}$$

From ref.[14] we find $\varepsilon^0_{Hg/HgO} = 0\cdot098$ V $(25°C)$, from Eqs (27) and (29) we calculate $\varepsilon^0_{H_2/OH^-}$ and a_{H_2O} at 25°C. The partial pressure of hydrogen, p_{H_2}, is determined according to Eq. (31) as in calculating E. The value of E' at other temperatures is obtained by integrating the equation

$$\partial(E'/T)/\partial T = \Delta H'_r/2FT^2\,. \tag{38}$$

The reaction enthalpy for the given cell reaction at 25°C is $\Delta H'_r = \Delta H^f_{H_2O} - H^f_{HgO} + \bar{L}_{H_2O}$. From ref.[8,28] we find $\Delta H^f_{H_2O} = -68317$ and $\Delta H^f_{HgO} = -21560\ cal/mol$ (25°C); $\bar{L}_{H_2O}$ is given by Eq. (10). The dependence of ΔH_r on temperature follows from the equation

$$\partial \Delta H'_r / \partial T = C_{p,Hg} + \bar{C}_{p,H_2O} - C_{p,H_2} - C_{p,HgO} . \tag{39}$$

From tabulated data[29] follows $C_{p,HgO} = 6.2664 + 0.01553T$; equations for the other quantities were already given. From Eqs (38) and (39) we obtain the resulting equation for the electromotive force:

$$E' = E'_{298}T/298.15 - (T/2F)\{(\bar{L}_{H_2O,298} - 44221)/T + 5.917 \ln T +$$

$$+ 8.685 . 10^{-3}T - \sum_{i=0}^{5} \left[1 - i(m/55.506 + 1)\right] m^i \left[z_{i0}(\ln T + 298.15/T) +\right.$$

$$\left.+ \sum_{j=1}^{4} z_{ij}(T^j/j + 298.15^{j+1}/T)/(j+1)\right]\}^T_{298.15} . \tag{40}$$

RESULTS AND DISCUSSION

The electromotive force of the amalgam–hydrogen cell and of the cell (D), reaction enthalpy of the decomposition reaction (A), partial relative molar enthalpy of water and logarithm of the water activity in the soda lye as well as partial pressure of hydrogen were calculated on an Elliott 503 computer for different technologically important temperatures and concentrations (Tables III and IV).

The electromotive force E of the amalgam–hydrogen cell is technically important, therefore we shall estimate the error inherent in its calculation from Eq. (30) and compare the calculated values with the literature data. First we note the validity ranges of the equations for the quantities used in deriving Eq. (30):

$$\gamma_{NaOH\pm,298}, a_{H_2O,298}: \qquad 0.4 \leqq p \leqq 53.7\ wt.\%$$

$$\Delta H^{rel}_{L,298}: \qquad p \leqq 48\ wt.\%$$

$$\bar{L}_{Na,298}, a_{Na,298}: \qquad N_{Na} \leqq 0.59\ wt.\%$$

$$\bar{C}_{p,Na}: \qquad N_{Na} \leqq 0.52\ wt.\%, 20 \leqq t \leqq 50°C$$

$$C_{p,L}: \qquad p \leqq 52\ wt.\%, 15.5 \leqq t \leqq 93.3°C$$

$$C_{p,H_2}: \qquad 0 \leqq t \leqq 100°C$$

Other quantities were used only in the range of temperatures and concentrations in which they were experimentally determined. Hence, the calculation of E from Eq.

(30) for $25 \leqq t \leqq 100°C$, $0 \leqq N_{Na} \leqq 0.5$ wt.% and $10 \leqq p \leqq 50$ wt.% (Table III) involves extrapolation of: *1)* $\bar{C}_{p,Na}$ from 50 to 100°C; according to Eq. (24) this value is at 100°C equal to 6·24 cal/mol K in good agreement with the Dulong-Petit rule; *2)* $C_{p,L}$ from 93·3 to 100°C; however, the temperature dependence of $C_{p,L}$ at $t > 90°C$ is small; *3)* $\Delta H_{L,298}^{rel}$ from 48 to 50 wt.% NaOH.

The error in the calculation of E_{298} is estimated as follows: The error in the difference $\varepsilon_{Na}^{0} - \varepsilon_{H_2/OH^-}^{0}$ at 25°C is about 0·6 mV, the error caused by Eq. (14) for a_{Na} is smaller than 0·1 mV (ref.[6]) and that due to the equations for $\gamma_{NaOH\pm,298}$ and $a_{H_2O,298}$ is estimated as 1·6 and 0·8 mV (based on the 3% difference between the activity coefficients in the literature[17,20]). The sum of these errors is $\delta E \approx 3.1$ mV, *i.e.*, the error in Eq. (30) for E due to E_{298} is equal to $(T/298.15)\delta E$.

Integration of the Gibbs–Helmholtz equation (2) introduces an additional error in E approximately equal to $(\delta\Delta H_r/F)(T/298.15 - 1)$, where $\delta\Delta H_r$ is the mean error in the reaction enthalpy ΔH_r in the interval from 298·15K to T; it is estimated as 800 cal/mol. Accordingly, the integration errors for $T = 333.15$, 353·15 and 373·15K are 4·1, 6·4 and 8·7 mV and the total errors in the electromotive force E are estimated

TABLE III

Electromotive Force of Amalgam–Hydrogen Cell According to Eq. (30)

Partial pressure of hydrogen calculated from Eq. (31), $p_T = 1$ atm. Values given in volts.

°C	wt.% NaOH	wt.% Na in amalgam				
		0·01	0·05	0·1	0·2	0·5
25	10	0·907	0·951	0·973	0·998	1·045
	20	0·829	0·874	0·895	0·921	0·967
	30	0·736	0·781	0·802	0·828	0·874
	40	0·631	0·675	0·697	0·723	0·769
	50	0·548	0·592	0·614	0·639	0·686
70	10	0·888	0·939	0·964	0·993	1·046
	20	0·807	0·859	0·883	0·913	0·965
	30	0·721	0·772	0·797	0·826	0·879
	40	0·629	0·680	0·705	0·734	0·787
	50	0·557	0·608	0·633	0·662	0·714
100	10	0·905	0·961	0·988	1·019	1·076
	20	0·811	0·866	0·893	0·925	0·981
	30	0·721	0·777	0·804	0·835	0·892
	40	0·632	0·687	0·714	0·746	0·803
	50	0·564	0·620	0·647	0·678	0·735

as 7·6, 10·1 and 12·6 mV, respectively. However, it is probable that in reality the accuracy is better since the individual errors can compensate partially one another.

Direct experimental data for the electromotive force of the amalgam–hydrogen cell, E, are not available in the literature. Equilibrium potentials of the amalgam and alkaline hydrogen electrode at $25 - 60°C$, $5 - 40$ wt.% NaOH and $0·007$ to $0·386$ wt.% Na were measured by Aoki and coworkers[21]. From their data we calculated values of E which differed from those according to Eq. (30) by 9·3 mV on the average; positive and negative deviations were practically equally significant. The values of E calculated by Balej using a simplified method[22] are on the average by 8 mV lower than those from Eq. (30), the largest difference (18 mV) being in the case of 50 wt.% NaOH.

Hine[24] presented an empirical equation for E valid in the range $50 - 90°C$, 10 to 50 wt.% NaOH and $0·017 - 0·337$ wt.% Na, which however leads to values of E differing by up to 83 mV from those calculated from Eq. (30) in this validity range. The low accuracy of Hine's equation was pointed out also by Burian[25]. The values
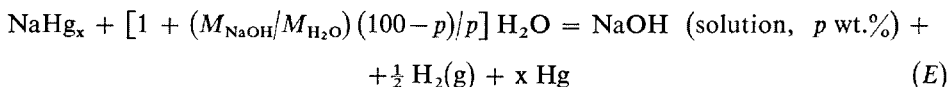
TABLE IV

Thermodynamic Quantities

Reaction enthalpy for amalgam decomposition, ΔH_r, from Eq. (25) for 0·2 wt.% Na; $\log a_{H_2O}$ from Eq. (35); p_{H_2O} from Eqs (35) and (36); values of E' for the cell $Pt|H_2|NaOH,H_2O|HgO|Hg$ from Eq. (40); $p_T = 1$ atm.

°C	NaOH	$-\Delta H_r$ cal/mol	L_{H_2O} cal/mol	$- \log a_{H_2O}$	p_{H_2O} atm	E' V
25	10	24 364	2·4	0·0465	0·0281	0·927
	20	23 214	−90	0·1445	0·0224	0·930
	30	19 880	−539	0·3514	0·0139	0·936
	40	15 148	−1 464	0·6971	0·0063	0·947
	50	11 342	−2 495	1·072	0·0027	0·958
70	10	24 543	−20	0·0457	0·2767	0·908
	20	22 825	−153	0·1329	0·2264	0·912
	30	19 456	−602	0·2965	0·1553	0·919
	40	15 128	−1 447	0·5566	0·0853	0·928
	50	11 565	−2 415	0·8355	0·0449	0·938
100	10	24 646	−35	0·0443	0·9023	0·863
	20	22 549	−194	0·1241	0·7510	0·881
	30	19 178	−642	0·2647	0·5432	0·896
	40	15 199	−1 418	0·4833	0·3284	0·910
	50	11 684	−2 378	0·7129	0·1936	0·921

of E tabulated by McMullin[23] are incorrect owing to an error in the underlying Nernst equation (1), where the term $(m\gamma_{NaOH\pm})^2$ was replaced by $m\gamma_{NaOH\pm}$.

As far as the reaction enthalpy of amalgam decomposition is concerned, an empirical formula for the reaction

$$NaHg_x + \left[1 + (M_{NaOH}/M_{H_2O})(100-p)/p\right] H_2O = NaOH \;(\text{solution}, \; p \text{ wt.\%}) +$$
$$+ \tfrac{1}{2} H_2(g) + x\,Hg \qquad\qquad (E)$$

in the range $25-100°C$ and $35-50$ wt.% NaOH was given by Charvát (cit. in[22]). For obtaining the values of ΔH_r of the reaction (A), it is necessary to add $\bar{L}_{H_2O}$ . . $\left[1 + (M_{NaOH}/M_{H_2O})(100\text{-}p)/p\right]$ to the values of Charvát's formula. For 50 wt% NaOH, 0·2 wt.% Na and 25°C, the difference between ΔH_r calculated according to the corrected Charvát's formula and Eq. (25) is only 52 cal/mol, for 100°C 348 cal/mol. The analogous results for 5% NaOH and 0·2 wt.% Na are 2470 and 9508 cal/mol. The latter differences are probably caused by the simple expressions for concentration dependence of ΔH_r in Charvát's formula.

LIST OF SYMBOLS

a_{Na}, a_{H_2O}	activities of sodium and water
a_i, b_i	constants in Eqs (9) and (28)
C_p	molar heat capacity (cal/mol K)
c_p	specific heat capacity (cal/g K)
c_i	constants in Eq. (29)
E, E'	electromotive force of cell (B) or (D) (V)
F	Faraday's constant (96497 C/mol)
f_m	parameter defined by Eq. (18)
H	molar enthalpy (cal/mol)
ΔH_{BC}	relative enthalpy of soda lye in ref.[1] referred to infinite dilution (BTU/1b of solution)
ΔH^f	enthalpy of formation (cal/mol)
ΔH_r, $\Delta H_r'$	reaction enthalpy for reactions (A) and that in cell (D) (cal/mol)
ΔH_1 through ΔH_5	reaction enthalpies for reactions (C_1) through (C_5) (cal/mol)
K_{H_2O}	equilibrium dissociation constant of water
$\bar{L}$	partial relative molar enthalpy, Eqs (3) and (4) (cal/mol)
M	molar mass (g/mol)
N_{Na}	concentration of sodium in amalgam (wt.%)
p	concentration of NaOH solution (wt.%)
p_T, p_{H_2}, p_{H_2O}	total pressure, partial pressure of hydrogen and equilibrium tension of water vapour above NaOH solution (atm)
R	gas constant (1·98719 cal/mol K)
T	absolute temperature (K)
t	Celsius temperature (°C)
X_{Na}	mole fraction of sodium in amalgam
z_{ij}	constants in Eq. (7)

$\gamma_{NaOH\pm}$ mean molal activity coefficient of NaOH
ε^0 standard electrode potential   (V)
Φ practical osmotic coefficient of NaOH solution

Superscript o denotes standard state, subscript 293 or 298 refers to temperature of 293·15 or 298·15 K. Partial molar quantities are distinguished by a bar above the symbol.

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