# ACTIVITY COEFFICIENTS OF AQUEOUS SOLUTIONS OF NaOH AND KOH IN WIDE CONCENTRATION AND TEMPERATURE RANGES 

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Up to now, there exist a quite wide temperature interval between 70 or 80 and $150{ }^{\circ} \mathrm{C}$ with no sufficiently reliable experimental data of mean activity coefficients for aqueous NaOH as well as KOH solutions. In order to fill this gap, it was tried to derive suitable correlation equations for this quantity in dependence on the molality (for NaOH in the range $m_{\mathrm{NaOH}}=2-25 \mathrm{~mol} \mathrm{~kg}^{-1}$, for KOH in the range $m_{\mathrm{KOH}}=2-18 \mathrm{~mol} \mathrm{~kg}^{-1}$ ) and temperature (in the range $0-200^{\circ} \mathrm{C}$ for both kinds of solutions) on the basis of the available data of this quantity and with the use of the previously derived correlation equations for the water activity in aqueous solutions of NaOH and KOH under the same conditions. The comparison between the calculated and experimental data was discussed.
Key words: Mean activity coefficient; Aqueous solutions; NaOH ; KOH.

For the thermodynamic calculation of the equilibrium states of chemical or electrochemical reactions with the participation of aqueous solutions of NaOH or KOH it is necessary to know their activities under real reaction conditions. The activity of a $1: 1$ electrolyte is usually expressed by the product of its total molality and the appropriate practical mean activity coefficient at the given molality and temperature, i.e. $a_{\mathrm{MeOH}}=$ $\left(m_{\mathrm{MeOH}} \gamma_{ \pm \mathrm{MeOH}}\right)^{2}$. The quantitative concentration and temperature dependence of the mean activity coefficients of aqueous solutions of strong electrolytes, based on the Debye-Hückel theory ${ }^{1-5}$, is mostly complicated. Some methods of theoretical calculations of activity coefficients (e.g. according to Pitzer ${ }^{6}$, Bromley ${ }^{7,8}$ or Messner ${ }^{9}$ ) give sufficiently reliable results for a limited range of concentrations only, e.g. for NaOH or KOH solutions in the range of $0-6 \mathrm{~mol} \mathrm{~kg}{ }^{-1}$ (ref. ${ }^{10}$ ). For various technical processes, however, even more concentrated solutions of sodium or potassium hydroxides are frequently used at temperatures less or more different from the reference temperature of $25^{\circ} \mathrm{C}$. Until now, however, the overall relations for the mean practical activity coefficients of aqueous solutions of NaOH or KOH valid in a necessary wide range of their molality as well as temperature are not available.

A critical evaluation of the all published sufficiently reliable data of the mean practical coefficients of aqueous solutions of NaOH and KOH at $25^{\circ} \mathrm{C}$ was presented by Hammer and Wu in 1972 (ref. ${ }^{11}$ ). The smoothed data were fitted with the aid of an extended Debye-Hückel equation

$$
\begin{equation*}
\log \gamma_{ \pm}=-A_{\gamma}\left|z_{+} z_{-}\right| I^{0.5} /\left(1+B I^{0.5}\right)+\beta I+C I^{2}+D I^{3}+\ldots, \tag{1}
\end{equation*}
$$

where $I$ stands for the ionic strength defined by the relation

$$
\begin{equation*}
I=0.5 \sum_{i=1}^{k} m_{i} z_{i}^{2} . \tag{2}
\end{equation*}
$$

$B, \beta, C$ and $D$ denote the specific constants for the given electrolyte at the given temperature, $z_{+}$and $z_{-}$are the charge numbers of the appropriate cation and anion, and $A_{\gamma}$ represents the temperature dependent value of the Pitzer-Debye-Hückel limiting slope for the activity coefficients in aqueous solutions (e.g. $A_{\gamma}=0.51084$ at $25^{\circ} \mathrm{C}$ (ref. ${ }^{11}$ ). It must, however, be mentioned that the value of this quantity changed a little as time went due to the progressive precision of the dielectric constant of water; its recent internationally recognized values may be calculated from the values of the limiting slopes for the osmotic coefficients, $A_{\Phi}$, for the range of $0-350^{\circ} \mathrm{C}$ and from saturation to $1 \mathrm{kbar}\left(\right.$ ref. ${ }^{12}$ ), using the relation $A_{\gamma}=3 A_{\Phi}$.

The mean activity coefficients of aqueous solutions of sodium and potassium hydroxides in dependence on their concentration and temperature were also determined several times. Harned and Hecker ${ }^{13}$ measured these values for $0.05-4.0 \mathrm{~m} \mathrm{NaOH}$ at $0-35^{\circ} \mathrm{C}$. Similar measurements for KOH solutions were published by Harned and Cook ${ }^{14}$. Analogous measurements for NaOH solutions at wider concentration as well as temperature ranges (i.e. $0.1-17 \mathrm{~mol} \mathrm{~kg}^{-1}$ ) were done by Akerlöf and Kegeles ${ }^{15}$ and for KOH solutions by Akerlöf and Bender ${ }^{16}$. Zarembo et al. ${ }^{17}$ published the data of the mean activity coefficients of $0.85-23.8 \mathrm{~m} \mathrm{NaOH}$ and $0.85-17.5 \mathrm{~m} \mathrm{KOH}$ solutions at $423-623 \mathrm{~K}$ (i.e. $150-350{ }^{\circ} \mathrm{C}$ ) in intervals of 50 K . Further data for $1-8 \mathrm{~m} \mathrm{NaOH}$ and KOH as well as for $1-5 \mathrm{~m} \mathrm{LiOH}$ solutions at -10 to $120^{\circ} \mathrm{C}$ were presented by Pound et al. ${ }^{18}$ in 1986. These data, however, exhibit an unusual course of the temperature dependence in the range of -10 to $40^{\circ} \mathrm{C}$ for NaOH solutions and -10 to $60^{\circ} \mathrm{C}$ for KOH solutions. Further, the numerical values of the activity coefficients at $60-80^{\circ} \mathrm{C}$ differ considerably from the values for the solutions of the same composition referred by other authors ${ }^{2,3,13-16}$, although their temperature trend is similar (see Figs 1 and 2). Moreover, values of $\gamma_{ \pm, \mathrm{KOH}}$ instead of $\log \gamma_{ \pm, \mathrm{KOH}}$ are most probably given for 263 K in Table 6 of ref. ${ }^{18}$. Therefore, neglecting the data of Pound et al. ${ }^{18}$ as unsufficiently reliable, it may be concluded that there exists a quite wide interval between $70-150{ }^{\circ} \mathrm{C}$ and $80-150 \mathrm{C}^{\circ} \mathrm{C}$ for NaOH and KOH solutions, respectively, with no sufficiently reliable values of the mean activity coefficients. It is, however, evident that a simple extrapolation of existing data into this temperature range is hardly possible, especially for lower solution concentrations. Only for NaOH solutions, it seems to be possible to
extrapolate high temperature data for $20-24 \mathrm{~m} \mathrm{NaOH}$ (ref. ${ }^{17}$ ) till down to $25^{\circ} \mathrm{C}$ where they coincide with the smoothed NBS data ${ }^{11}$ at this temperature. Therefore, in order to gain sufficiently reliable data of the mean activity coefficients of NaOH and KOH solutions in the whole wanted range of molalities and temperatures, it is necessary either to undertake new experimental measurements or to try to correlate all till available experimental data in a proper way for the whole range of molalities and temperatures as well. It must, however, be taken into account that such a correlation can lead to an expression with a lower reliability grade. The latter method presents the subject of this communication.

Fig. 1
Temperature dependence of $\log \gamma_{ \pm}$for various molalities of aqueous sodium hydroxide solutions: $+\left(\right.$ ref. $\left.^{11}\right), \quad\left(\right.$ refs $\left.^{15,17}\right),-\cdot-\cdot-$ (ref. ${ }^{18}$ )


Fig. 2
Temperature dependence of $\log \gamma_{ \pm}$for various molalities of aqueous potassium hydroxide solutions: $+\left(\right.$ ref. $\left.{ }^{11}\right),-\quad\left(\right.$ refs $\left.^{16,17}\right),-\cdot-\cdot$ (ref. ${ }^{18}$ )


## RESULTS AND DISCUSSION

The derivation of the correlation equation for $\log \gamma_{ \pm}=f\left(m_{\mathrm{MeOH}}, T\right)$ was based on the well known relations between the activity of water, $a_{\mathrm{w}}$, in the aqueous electrolyte solution of molality $m_{1}$ and its osmotic ( $\Phi$ ) and mean activity coefficient $\gamma_{ \pm}$(e.g. refs ${ }^{2,19}$ ):

$$
\begin{equation*}
\Phi=-1000 \ln a_{\mathrm{w}} /\left(M_{\mathrm{w}} v_{\mathrm{i}} m_{\mathrm{i}}\right) \tag{3}
\end{equation*}
$$

and

$$
\begin{equation*}
\ln \gamma_{ \pm}=\Phi-1+2 \int_{0}^{m}\left((\Phi-1) / m^{0.5}\right) \mathrm{d} m^{0.5} . \tag{4}
\end{equation*}
$$

Here, $M_{\mathrm{w}}$ denotes the molar weight of water and $v_{\mathrm{i}}$ the total amount of ions of the given electrolyte. In the given case, $M_{\mathrm{w}}=18.01528 \mathrm{~g} \mathrm{~mol}^{-1}, v_{\mathrm{MeOH}}=2$, so that

$$
\begin{equation*}
\Phi=\left(-27.75422 / m_{\mathrm{MeOH}}\right) \ln a_{\mathrm{w}}=\left(-63.90645 / m_{\mathrm{MeOH}}\right) \log a_{\mathrm{w}} . \tag{5}
\end{equation*}
$$

The following relations have been derived in a previous paper ${ }^{20}$ for the molality and temperature dependence of the water activity in aqueous solutions of NaOH and KOH (using data in the above mentioned papers ${ }^{14-16}$ ):

$$
\begin{align*}
\log a_{\mathrm{w}(\mathrm{NaOH})}= & -0.01332 m+0.002542 m^{2}-3.06 \cdot 10^{-5} m^{3}+ \\
& +\left(1.5827 m-1.5669 m^{2}+0.021296 m^{3}\right) / T \tag{6}
\end{align*}
$$

This equation is valid for $m_{\mathrm{NaOH}}=2-25 \mathrm{~mol} \mathrm{~kg}^{-1}$ (i.e. $7.4-50 \mathrm{wt} . \% \mathrm{NaOH}$ ) and for $T=$ 273.15-473.15 K.

For KOH solutions

$$
\begin{equation*}
\log a_{\mathrm{w}(\mathrm{KOH})}=-0.02255 m+0.001434 m^{2}+\left(1.38 m-0.9254 m^{2}\right) / T, \tag{7}
\end{equation*}
$$

valid for $m_{\mathrm{KOH}}=2-18 \mathrm{~mol} \mathrm{~kg}^{-1}$ (i.e. $10-50 \mathrm{wt} . \% \mathrm{KOH}$ ) and for the same temperature range, 273.15-473.15 K.

Due to the validity of Eqs (6) and (7) in limited molality ranges it is necessary to transform Eq. (3) for a limited range, too:

$$
\begin{equation*}
\ln \gamma_{ \pm}=\ln \gamma_{ \pm 1}+\Phi-\Phi_{1}+2 \int_{m_{1}}^{m_{2}}\left((\Phi-1) / m^{0.5}\right) \mathrm{d} m^{0.5} \tag{8}
\end{equation*}
$$

or

$$
\begin{equation*}
\log \gamma_{ \pm}=\log \gamma_{ \pm 1}+\left(\Phi-\Phi_{1}\right) /(\ln 10)+(2 /(\ln 10)) \int_{m_{1}}^{m_{2}}\left((\Phi-1) / m^{0.5}\right) \mathrm{d} m^{0.5}, \tag{9}
\end{equation*}
$$

where $\gamma_{ \pm 1}$ and $\Phi_{1}$ are the known values of the mean activity and osmotic coefficients of the MeOH solution at the lower limit of the concentration range, $m_{\mathrm{MeOH}, 1}=2 \mathrm{~mol} \mathrm{~kg}^{-1}$,
and the given temperature. Combining Eq. (5) with Eq. (6) or (7) the following relations were obtained for the concentration and temperature dependence of the osmotic coefficients:

$$
\begin{align*}
\Phi_{\mathrm{NaOH}}= & 0.8512339-101.1447 / T-(0.16245019-100.135 / T) m+ \\
& +(0.001955537-1.360952 / T) m^{2}, \tag{10}
\end{align*}
$$

valid for $m_{\mathrm{NaOH}}=2-25 \mathrm{~mol} \mathrm{~kg}^{-1}$ and $T=273.15-473.15 \mathrm{~K}$ and

$$
\begin{equation*}
\Phi_{\mathrm{KOH}}=1.4410904-88.190898 / T-(0.09164185-59.13909 / T) m, \tag{11}
\end{equation*}
$$

valid for $m_{\mathrm{KOH}}=2-18 \mathrm{~mol} \mathrm{~kg}^{-1}$ and the same temperature range, $273.15-473.15 \mathrm{~K}$.
For the lower limit of $m_{\mathrm{MeOH}, 1}=2 \mathrm{~mol} \mathrm{~kg}^{-1}$, Eqs (10) and (11) became simplified forms, namely

$$
\begin{equation*}
\Phi_{\mathrm{NaOH}, 1}=0.5341556+93.68149 / T \tag{12}
\end{equation*}
$$

and

$$
\begin{equation*}
\Phi_{\text {КОН }, 1}=1.257807+30.08716 T . \tag{13}
\end{equation*}
$$

In order to obtain the temperature dependence of the activity coefficients of NaOH or KOH solutions for the molality $m_{\mathrm{NaOH}}=2 \mathrm{~mol} \mathrm{~kg}^{-1}$ in the temperature range of $273.15-473.15 \mathrm{~K}$, it was necessary to obtain a suitable correlation equation for the temperature dependence of the mean practical activity coefficients $\gamma_{ \pm, 1}$ at $m_{\mathrm{MeOH}, 1}=$ $2 \mathrm{~mol} \mathrm{~kg}{ }^{-1}$. This correlation was obtained by evaluating all available experimental data in $\mathrm{refs}^{2,11-13,15,17}$ and in refs ${ }^{2,11,12,14,16,17}$ for 2 m NaOH and 2 m KOH , respectively. The only two available experimental data at 150 and $200^{\circ} \mathrm{C}$ for both kinds of solutions were supplemented by numerical interpolation for intervals of 10 K on the basis of the following relations derived now on the basis of experimental data for the range of $150-350{ }^{\circ} \mathrm{C}$ (ref. ${ }^{17}$ ) for 2 m NaOH solution:

$$
\begin{equation*}
\log \gamma_{ \pm}=-82.917+0.68171 T-0.0020924 T^{2}+2.83734 \mathrm{E}-6 T^{3}-1.44 \mathrm{E}-9 T^{4} \tag{14}
\end{equation*}
$$

and for 2 m KOH solution (see Fig. 3):

$$
\begin{equation*}
\log \gamma_{ \pm}=-82.722+0.68171 T-0.0020924 T^{2}+2.83734 \mathrm{E}-6 T^{3}-1.44 \mathrm{E}-9 T^{4} \tag{15}
\end{equation*}
$$

Using the least-square method the following polynomic relations were obtained on the basis of all selected available data for the temperature range $T=273.15-473.15 \mathrm{~K}$. For the correlation of all available experimental data the polynom of the 6th order was used; it was therefore necessary to express all coefficients with $8-9$ significant digits. Then, for 2 m NaOH solution:

$$
\begin{align*}
\log \gamma_{ \pm}= & 175.972176-2.98871232 T+0.0208479756 T^{2}- \\
& -7.65562053 \mathrm{E}-5 T^{3}+1.5619109 \mathrm{E}-7 T^{4}- \\
& -1.68003492 \mathrm{E}-10 T^{5}+7.44709291 \mathrm{E}-14 T^{6} \tag{16}
\end{align*}
$$

and for 2 m KOH solution:

$$
\begin{align*}
\log \gamma_{ \pm}= & 473.494301-8.17278423 T+0.0581847419 T^{2}- \\
& -2.18641894 \mathrm{E}-4 T^{3}+4.57270983 \mathrm{E}-7 T^{4}- \\
& -5.04647259 \mathrm{E}-10 T^{5}+2.29069204 \mathrm{E}-13 T^{6} . \tag{17}
\end{align*}
$$

The agreement of the so calculated and experimental data of 2 m NaOH as well as 2 m KOH solutions may be held as good (see Fig. 4, where the course of the calculated values in the whole considered temperature range is depicted by full lines).

Inserting Eqs (10), (12) and (16) into Eq. (9), one obtains after integration and rearrangement, the final relation for the concentration and temperature dependence of the mean practical activity coefficient of aqueous NaOH solutions,

$$
\begin{align*}
\log \gamma_{ \pm, \mathrm{NaOH}}= & 176.2940683-139.958399 / T-2.98871232 T+0.0208479756 T^{2}- \\
& -7.65562053 \mathrm{E}-5 T^{3}+1.5619109 \mathrm{E}-7 T^{4}-1.68003492 \mathrm{E}-10 T^{5}+ \\
& +7.44709291 \mathrm{E}-14 T^{6}-(0.141102442-86.97615589 / T) m+ \\
& +(0.001273918392-0.886580916 T) m^{2}- \\
& -(0.14876612+101.4477 / T) \log m, \tag{18}
\end{align*}
$$

valid for $m_{\mathrm{NaOH}}=2-25 \mathrm{~mol} \mathrm{~kg}$-1 and $T=273.15-473.15 \mathrm{~K}$.


Fig. 3
Temperature dependence of $\log \gamma_{ \pm}$of 2 m NaOH (1) and KOH (2) solutions in the range $150-350{ }^{\circ} \mathrm{C}$ : after ref. ${ }^{17}$ for NaOH (x) and $\mathrm{KOH}(+)$; calculated from Eqs (14) and (15), respectively ( - )

In a similar manner, after the insertion of Eqs (11), (13) and (17) into Eq. (9) and subsequent integration and rearrangement, the following expression for the concentration and temperature dependence of the mean practical activity coefficient of aqueous KOH solutions was obtained,

$$
\begin{align*}
\log \gamma_{ \pm, \mathrm{KOH}}= & 473.5207145-76.18691014 T-8.17278423 T+0.05818474219 T^{2}- \\
& -2.18641894 \mathrm{E}-4 T^{3}+4.57270983 \mathrm{E}-7 T^{4}-5.04647259 \mathrm{E}-10 T^{5}+ \\
& +2.29609204 \mathrm{E}-13 T^{6}-(0.0795991-51.36750792 / T) m+ \\
& +(0.4410904-88.190898 / T) \log m, \tag{19}
\end{align*}
$$

valid for $m_{\mathrm{KOH}}=2-18 \mathrm{~mol} \mathrm{~kg}^{-1}$ and $T=273.15-473.15 \mathrm{~K}$.
A comparison of the so calculated values of decadic logarithms of the mean molal activity coefficients with experimental data for NaOH solutions according to refs ${ }^{11,15,17}$ and KOH solutions according to refs ${ }^{11,16,17}$ is given in Tables I and II. As may be seen, quite good agreement between both kinds of values may be observed for KOH solutions at almost the whole considered range of molalities and temperatures, while for NaOH solutions the deviations are somewhat more evident at temperatures lower than $25^{\circ} \mathrm{C}$. With respect to the numerical scatter of experimental results of various authors (see e.g. Figs 1-4), the obtained relations (18) and (19) can therefore be considered as sufficiently reliable for the calculation of the mean activity coefficients of aqueous NaOH and KOH solutions in dependence on their concentration in the range $m_{\mathrm{NaOH}}=2-25$ and $m_{\mathrm{KOH}}=2-18 \mathrm{~mol} \mathrm{~kg}^{-1}$ and temperature range $0-200{ }^{\circ} \mathrm{C}$. In addition, calculated data represent suitable continuous supplementation of lacking experimental data in the temperature range 70 or 80 and $150^{\circ} \mathrm{C}$. They may find a good application especially for solving various equilibrium problems in technically important systems containing

Fig. 4
Temperature dependence of $\log \gamma_{ \pm}$of 2 m NaOH (1) and KOH (2) solutions in the range $0-200{ }^{\circ} \mathrm{C} ; \mathrm{NaOH}: \Delta$ (ref. ${ }^{11}$ ), $+\left(\right.$ ref. $\left.{ }^{13}\right), \times\left(\right.$ ref. ${ }^{15}$ ), $\square$ (ref. ${ }^{17}$ ); KOH : O (ref. ${ }^{2}$ ), $\mathbf{\Delta}\left(\right.$ ref. $\left.^{11}\right)$, $\bigcirc\left(\right.$ ref. ${ }^{14}$ ), (ref. ${ }^{16}$ ), ■ (ref. ${ }^{17}$ ); ——calculated from Eqs (16) and (17), respectively

Table I
Calculated (upper data, Eq. (18)) and experimental values (lower data, $0-70{ }^{\circ} \mathrm{C}$ (ref. ${ }^{15}$ ), $25^{\circ} \mathrm{C}$ (ref. ${ }^{11}$ ), $150-200{ }^{\circ} \mathrm{C}$ (ref. ${ }^{17}$ ) of $\log \gamma_{ \pm}$of aqueous NaOH solutions in the range of $m_{\mathrm{NaOH}}=2-24 \mathrm{~mol} \mathrm{~kg}^{-1}$ and temperature $t=0-200^{\circ} \mathrm{C}$

| $t,{ }^{\circ} \mathrm{C}$ | $m_{\mathrm{NaOH}}, \mathrm{~mol} \mathrm{~kg}^{-1}$ |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 | 20 | 22 | 24 |
| 0 | $-0.1685$ | +0.0058 | 0.2294 | 0.4639 | 0.6971 | 0.9238 | 1.1411 | 1.3472 | 1.5412 | 1.7221 | 1.8896 | 2.0432 |
|  | -0.1664 | -0.0458 | 0.1438 | 0.3718 | 0.6153 | 0.8547 | 1.0553 | 1.2528 | 1.4502 | - | - | - |
| 10 | $-0.1613$ | -0.0041 | 0.2017 | 0.4185 | 0.6346 | 0.8449 | 1.0465 | 1.2378 | 1.4177 | 1.5855 | 1.7407 | 1.8828 |
|  | -0.1539 | -0.0360 | 0.1451 | 0.3646 | 0.5994 | 0.8242 | 1.0003 | 1.1858 | 1.3713 | - | - | - |
| 20 | -0.1514 | -0.0139 | 0.1751 | 0.3755 | 0.5757 | 0.7707 | 0.9577 | 1.1352 | 1.3021 | 1.4575 | 1.6012 | 1.7327 |
|  | -0.1495 | -0.0382 | 0.1309 | 0.3372 | 0.5578 | 0.7633 | 0.9388 | 1.1125 | 1.2861 | - | - | - |
| 25 | $-0.1533$ | -0.0197 | 0.1614 | 0.3540 | 0.5466 | 0.7344 | 0.9145 | 1.0854 | 1.2460 | 1.3957 | 1.5339 | 1.6603 |
|  | -0.1464 | -0.0403 | 0.1147 | 0.3050 | 0.5130 | 0.7194 | 0.9076 | 1.0664 | 1.1922 | 1.2881 | 1.3622 | 1.4236 |
| 30 | $-0.1526$ | $-0.0263$ | 0.1472 | 0.3322 | 0.5175 | 0.6982 | 0.8717 | 1.0362 | 1.1908 | 1.3349 | 1.4678 | 1.5893 |
|  | -0.1475 | -0.0406 | 0.1189 | 0.3134 | 0.5205 | 0.7085 | 0.8710 | 1.0329 | 1.1947 | - | - | - |
| 40 | $-0.1545$ | $-0.0422$ | 0.1167 | 0.2873 | 0.4587 | 0.6261 | 0.7867 | 0.9392 | 1.0824 | 1.2157 | 1.3386 | 1.4508 |
|  | -0.1503 | -0.0479 | 0.1028 | 0.2847 | 0.4765 | 0.6469 | 0.7967 | 0.9469 | 1.0970 | - | - | - |
| 50 | -0.1609 | -0.0617 | 0.0835 | 0.2407 | 0.3990 | 0.5538 | 0.7025 | 0.8436 | 0.9761 | 1.0993 | 1.2128 | 1.3162 |
|  | -0.1573 | -0.0594 | 0.0828 | 0.2517 | 0.4266 | 0.5786 | 0.7161 | 0.8546 | 0.9930 | - | - | - |
| 60 | $-0.1710$ | -0.0842 | 0.0482 | 0.1927 | 0.3387 | 0.4817 | 0.6192 | 0.7496 | 0.8720 | 0.9858 | 1.0904 | 1.1856 |
|  | -0.1695 | -0.0760 | 0.0582 | 0.2133 | 0.3699 | 0.5036 | 0.6292 | 0.7560 | 0.8829 | - | - | - |

Table I

| $t,{ }^{\circ} \mathrm{C}$ | $m_{\mathrm{NaOH},} \mathrm{mol} \mathrm{kg}^{-1}$ |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 | 20 | 22 | 24 |
| 70 | -0.1839 | -0.1086 | 0.0116 | 0.1442 | 0.2787 | 0.4106 | 0.5374 | 0.6578 | 0.7707 | 0.8756 | 0.9719 | 1.0593 |
|  | -0.1858 | -0.0969 | 0.0298 | 0.1708 | 0.3075 | 0.4226 | 0.5358 | 0.6511 | 0.7664 | - | - | - |
| 80 | -0.1983 | -0.1340 | -0.0252 | 0.0961 | 0.2197 | 0.3412 | 0.4580 | 0.5689 | 0.6729 | 0.7693 | 0.8578 | 0.9379 |
|  | - | - | - | - | - | - | - | - | - | - | - | - |
| 90 | -0.2132 | -0.1593 | -0.0613 | 0.0494 | 0.1627 | 0.2742 | 0.3816 | 0.4836 | 0.5791 | 0.6676 | 0.7486 | 0.8218 |
|  | - | - | - | - | - | - | - | - | - | - | - | - |
| 100 | -0.2280 | -0.1839 | -0.0960 | 0.0045 | 0.1081 | 0.2102 | 0.3087 | 0.4022 | 0.4897 | 0.5707 | 0.6447 | 0.7114 |
|  | - | - | - | - | - | - | - | - | - | - | - | - |
| 110 | -0.2422 | -0.2073 | -0.1292 | $-0.0382$ | 0.0561 | 0.1494 | 0.2395 | 0.3249 | 0.4048 | 0.4787 | 0.5460 | 0.6065 |
|  | - | - | - | - | - | - | - | - | - | - | - | - |
| 120 | -0.2558 | -0.2298 | -0.1608 | -0.0788 | 0.0067 | 0.0916 | 0.1736 | 0.2514 | 0.3241 | 0.3912 | 0.4522 | 0.5068 |
|  | - | - | - | - | - | - | - | - | - | - | - | - |
| 130 | -0.2692 | -0.2516 | -0.1913 | -0.1180 | $-0.0408$ | 0.0361 | 0.1104 | 0.1810 | 0.2469 | 0.3075 | 0.3625 | 0.4115 |
|  | - | - | - | - | - | - | - | - | - | - | - | - |

Table I
(Continued)

| $t,{ }^{\circ} \mathrm{C}$ | $m_{\mathrm{NaOH}}, \mathrm{mol} \mathrm{kg}{ }^{-1}$ |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 | 20 | 22 | 24 |
| 140 | -0.2832 | -0.2735 | -0.2216 | -0.1564 | -0.0872 | -0.0179 | 0.0492 | 0.1128 | 0.1722 | 0.2267 | 0.2760 | 0.3197 |
|  | - | - | - | - | - | - | - | - | - | - | - | - |
| 150 | -0.2987 | -0.2963 | -0.2526 | -0.1952 | -0.1336 | -0.0716 | -0.0114 | 0.0457 | 0.0988 | 0.1475 | 0.1913 | 0.2300 |
|  | -0.227 | -0.253 | -0.213 | -0.164 | -0.112 | -0.056 | 0.000 | 0.055 | 0.110 | 0.157 | 0.197 | 0.230 |
| 160 | $-0.3167$ | -0.3219 | $-0.2854$ | -0.2355 | -0.1810 | -0.1260 | -0.0724 | -0.0216 | 0.0257 | 0.0688 | 0.1074 | 0.1412 |
|  | - | - | - | - | - | - | - | - | - | - | - | - |
| 170 | -0.3380 | -0.3501 | -0.3208 | -0.2780 | -0.2304 | -0.1820 | -0.1347 | -0.0899 | -0.0483 | 0.0105 | 0.0232 | 0.0524 |
|  | - | - | - | - | - | - | - | - | - | - | - | - |
| 180 | -0.3628 | -0.3815 | -0.3591 | -0.3231 | -0.2822 | -0.2400 | -0.1988 | -0.1597 | -0.1235 | -0.0908 | -0.0618 | -0.0371 |
|  | - | - | - | - | - | - | - | - | - | - | - | - |
| 190 | -0.3908 | -0.4159 | -0.4000 | -0.3705 | -0.3359 | -0.2998 | -0.2643 | -0.2307 | -0.1997 | -0.1718 | -0.1474 | -0.1268 |
|  | - | - | - | - | - | - | - | - | - | - | - | - |
| 200 | $-0.4202$ | -0.4513 | $-0.4418$ | -0.4186 | -0.3899 | -0.3596 | -0.3297 | -0.3013 | -0.2752 | -0.2520 | -0.2320 | -0.2154 |
|  | -0.431 | -0.450 | -0.440 | -0.422 | -0.398 | -0.371 | -0.345 | -0.319 | -0.292 | -0.270 | -0.250 | -0.228 |

Table II
Calculated (upper data, Eq. (19)) and experimental values (lower data, $0-70{ }^{\circ} \mathrm{C}\left(\right.$ ref..$^{16}$ ), $25{ }^{\circ} \mathrm{C}\left(\right.$ ref. ${ }^{11}$ ), $150-200{ }^{\circ} \mathrm{C}$ (ref. ${ }^{17}$ ) of $\log \gamma_{ \pm}$of aqueous KOH solutions in the range of $m_{\mathrm{KOH}}=2-18 \mathrm{~mol} \mathrm{~kg}^{-1}$ and temperature $t=0-200{ }^{\circ} \mathrm{C}$

| $t,{ }^{\circ} \mathrm{C}$ | $m_{\text {KOH }}, \mathrm{mol} \mathrm{~kg}^{-1}$ |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 |
| 0 | $-0.0532$ | 0.1993 | 0.4371 | 0.6688 | 0.8971 | 1.1234 | 1.3482 | 1.5720 | 1.7950 |
|  | -0.0590 | 0.1422 | 0.3846 | 0.6401 | 0.8923 | 1.1316 | 1.3550 | 1.5657 | 1.7728 |
| 10 | -0.0550 | 0.1876 | 0.4141 | 0.6339 | 0.8501 | 1.0640 | 1.2763 | 1.4874 | 1.6977 |
|  | -0.0576 | 0.1394 | 0.3727 | 0.6167 | 0.8569 | 1.0849 | 1.2982 | 1.4998 | 1.6981 |
| 20 | -0.0558 | 0.1777 | 0.3937 | 0.6024 | 0.8073 | 1.0096 | 1.2103 | 1.4097 | 1.6081 |
|  | $-0.0596$ | 0.1320 | $0.3560$ | $0.5891$ | $0.8180$ | $1.0354$ | 1.2392 | 1.4322 | 1.6219 |
| 25 | $-0.0573$ | 0.1719 | 0.3828 | 0.5863 | 0.7858 | 0.9827 | 1.1778 | 1.3716 | 1.5644 |
|  | $-0.0656$ | $0.1242$ | $0.3389$ | $0.5625$ | $0.7860$ | $1.0021$ | 1.2043 | 1.3863 | $1.5422$ |
| 30 | -0.0599 | 0.1650 | 0.3711 | 0.5696 | 0.7638 | 0.9554 | 1.1452 | 1.3336 | 1.5209 |
|  | -0.0646 | 0.1204 | 0.3351 | 0.5576 | 0.7759 | 0.9835 | 1.1784 | 1.3629 | 1.5437 |
| 40 | $-0.0687$ | 0.1481 | 0.3451 | 0.5339 | 0.7182 | 0.8997 | 1.0793 | 1.2574 | 1.4344 |
|  | $-0.0728$ | $0.1046$ | $0.3097$ | $0.5220$ | $0.7305$ | $0.9290$ | $1.1153$ | 1.2913 | 1.4624 |
| 50 | -0.0814 | 0.1280 | 0.3163 | 0.4960 | 0.6711 | 0.8431 | 1.0131 | 1.1815 | 1.3489 |
|  | -0.0833 | 0.0855 | 0.2808 | 0.4834 | 0.6827 | 0.8726 | 1.0508 | 1.2180 | 1.3783 |

Table II
(Continued)

| $t,{ }^{\circ} \mathrm{C}$ | $m_{\mathrm{KOH}}, \mathrm{mol} \mathrm{kg}^{-1}$ |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 |
| 60 | -0.0958 | 0.1065 | 0.2868 | 0.4580 | 0.6242 | 0.7874 | 0.9484 | 1.1078 | 1.2660 |
|  | -0.0968 | 0.0624 | 0.2478 | 0.4409 | 0.6316 | 0.8136 | 0.9839 | 1.1419 | 1.2896 |
| 70 | -0.1094 | 0.0862 | 0.2588 | 0.4220 | 0.5800 | 0.7348 | 0.8873 | 1.0382 | 1.1878 |
|  | -0.1120 | 0.0368 | 0.2121 | 0.3960 | 0.5787 | 0.7535 | 0.9161 | 1.0642 | 1.1973 |
| 80 | -0.1201 | 0.0693 | 0.2345 | 0.3903 | 0.5405 | 0.6874 | 0.8319 | 0.9747 | 1.1162 |
|  | - | - | - | - | - | - | - | - | - |
| 90 | $-0.1263$ | 0.0572 | 0.2158 | 0.3642 | 0.5071 | 0.6465 | 0.7835 | 0.9187 | 1.0526 |
|  | - | - | - | - | - | - | - | - | - |
| 100 | $-0.1273$ | 0.0542 | 0.2026 | 0.3443 | 0.4803 | 0.6126 | 0.7424 | 0.8704 | 0.9970 |
|  | - | - | - | - | - | - | - | - | - |
| 110 | $-0.1240$ | 0.0485 | 0.1945 | 0.3298 | 0.4592 | 0.5848 | 0.7079 | 0.8290 | 0.9488 |
|  | - | - | - | - | - | - | - | - | - |
| 120 | -0.1179 | 0.0495 | 0.1898 | 0.3190 | 0.4421 | 0.5614 | 0.6780 | 0.7927 | 0.9059 |
|  | - | - | - | - | - | - | - | - | - |

Table II
(Continued)

| $t,{ }^{\circ} \mathrm{C}$ | $m_{\mathrm{KOH}}, \mathrm{~mol} \mathrm{~kg}^{-1}$ |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 |
| 130 | -0.1116 | 0.0510 | 0.1858 | 0.3092 | 0.4264 | 0.5396 | 0.6501 | 0.7587 | 0.8657 |
|  | - | - | - | - | - | - | - | - | - |
| 140 | -0.1083 | 0.0497 | 0.1793 | 0.2972 | 0.4087 | 0.5162 | 0.6209 | 0.7236 | 0.8247 |
|  | - | - | - | - | - | - | - | - | - |
| 150 | -0.1111 | 0.0426 | 0.1671 | 0.2798 | 0.3859 | 0.4879 | 0.5871 | 0.6842 | 0.7797 |
|  | -0.107 | 0.025 | 0.155 | 0.288 | 0.400 | 0.510 | 0.604 | 0.699 | 0.780 |
| 160 | -0.1226 | 0.0269 | 0.1467 | 0.2544 | 0.3554 | 0.4522 | 0.5460 | 0.6378 | 0.7279 |
|  | - | - | - | - | - | - | - | - | - |
| 170 | -0.1436 | 0.0019 | 0.1171 | 0.2200 | 0.3161 | 0.4079 | 0.4967 | 0.5834 | 0.6684 |
|  | - | - | - | - | - | - | - | - | - |
| 180 | -0.1728 | -0.0310 | 0.0799 | 0.1782 | 0.2696 | 0.3566 | 0.4406 | 0.5224 | 0.6026 |
|  | - | - | - | - | - | - | - | - | - |
| 190 | -0.2046 | -0.0665 | 0.0403 | 0.1342 | 0.2212 | 0.3036 | 0.3830 | 0.4602 | 0.5356 |
|  | - | - | - | - | - | - | - | - | - |
| 200 | -0.2286 | -0.0940 | 0.0088 | 0.0985 | 0.1811 | 0.2592 | 0.3342 | 0.4069 | 0.4779 |
|  | -0.230 | -0.123 | -0.020 | 0.073 | 0.152 | 0.232 | 0.306 | 0.386 | 0.455 |

aqueous NaOH or KOH solutions under the given reaction conditions. For the most exact calculations it is evidently necessary to use new values of this quantity which are to be determined with the use of an exact as possible method within the whole range of the reaction conditions.

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