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Abstract

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THEORETICAL CALCULATION OF THE E.M.F. OF GALVANIC CELLS WITH MOLTEN SALT ELECTROLYTES, USING AS AN EXAMPLE

$\mathrm{Be_{(s)}|BeCl_{\mathit{n}}}$ + **molten** $\mathrm{KCl|Cl_{2(g)}, C_{(gr)}}$

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The e.m.f. of galvanic cells under equilibrium conditions is determined by the change in Gibbs energy ΔG in the reactions underlying their operation. Thus, in the cell $\mathrm{Be_{(s)}/BeCl_{\mathit{n}}}$ + molten $\mathrm{KCl|Cl_{2(g)}, C_{(gr)}}$, two parallel reactions take place:

$$\mathrm{Be_{(s)}} + \frac{1}{2}\mathrm{Cl_{2(g)}} = \mathrm{Be^{+}_{(melt)}} + \mathrm{Cl^{-}_{(melt)}}; \tag{I}$$

$$\mathrm{Be_{(s)}} + \mathrm{Cl_{2(g)}} = \mathrm{Be^{2+}_{(melt)}} + 2\mathrm{Cl^{-}_{(melt)}}, \tag{II}$$

the products of which are formed not in pure form, but as ions in the melt. For the first of these,

$$\Delta G_1 = \left[\Delta H^0_{\mathrm{Be^{+}_{(melt)}}} + \Delta H^0_{\mathrm{Cl^{-}_{(melt)}}}\right] - T\left[S^0_{\mathrm{Be^{+}_{(melt)}}} + S^0_{\mathrm{Cl^{-}_{(melt)}}} - S^0_{\mathrm{Be_{(s)}}} - \frac{1}{2}S^0_{\mathrm{Cl_{2(g)}}}\right], \tag{1}$$

and for the second,

$$\Delta G_2 = \left[\Delta H^0_{\mathrm{Be^{2+}_{(melt)}}} + 2\Delta H^0_{\mathrm{Cl^{-}_{(melt)}}}\right] - T\left[S^0_{\mathrm{Be^{2+}_{(melt)}}} + 2S^0_{\mathrm{Cl^{-}_{(melt)}}} - S^0_{\mathrm{Be_{(s)}}} - S^0_{\mathrm{Cl_{2(g)}}}\right]. \tag{2}$$

The e.m.f. of the cell is equal to $\mathcal{E} = -\frac{\Delta G_1}{23062} = -\frac{\Delta G_2}{46124}$ volts. To find it, one must know the standard values of the partial enthalpies ΔH^0 and entropies S^0 of beryllium and chlorine ions in the melt. They can be calculated with the aid of two coupled cycles:

$$\begin{array}{cccc}
 & \multicolumn{2}{c}{\underline{\hspace{12em}}} & \\
 & \multicolumn{2}{c}{\mathcal{E}} & \\
\downarrow & & & \downarrow \\
\mathrm{Be}_{(s)} \rightarrow \mathrm{Be}^{n+}_{(melt)}, & n\,\mathrm{Cl}^{-}_{(melt)} \leftarrow \frac{n}{2}\mathrm{Cl}_{2(g)}, & \mathrm{C}_{(gr)} & \\
\downarrow & \uparrow & \uparrow & \downarrow \\
\mathrm{Be}_{(g)} \rightarrow \mathrm{Be}^{n+}_{(g)}, & n\,\mathrm{Cl}^{-}_{(g)} \leftarrow n\,\mathrm{Cl}_{(g)} & &
\end{array}$$

The first of them includes the sublimation of beryllium ($\Delta H^0_{\mathrm{sub\,Be}_{(s)}}$, $\Delta S^0_{\mathrm{sub\,Be}_{(s)}}$), the ionization of its atomic vapors to singly or doubly charged ions ($\Delta H^0_{n-\mathrm{ioniz\,Be}_{(g)}}$, $\Delta S^0_{n-\mathrm{ioniz\,Be}_{(g)}}$), and the dissolution of gaseous beryllium ions in the KCl melt ($\Delta H^0_{\mathrm{diss\,Be}^{n+}_{(g)}}$, $\Delta S^0_{\mathrm{diss\,Be}^{n+}_{(g)}}$), where

$$\Delta H^0_{\mathrm{Be}^{n+}_{(melt)}} = \Delta H^0_{\mathrm{sub\,Be}_{(s)}} + \Delta H^0_{n-\mathrm{ioniz\,Be}_{(g)}} + \Delta H^0_{\mathrm{diss\,Be}^{n+}_{(g)}}$$

and

$$S^0_{\mathrm{Be}^{n+}_{(melt)}} = S^0_{\mathrm{Be}_{(s)}} + \Delta S^0_{\mathrm{sub\,Be}_{(s)}} + \Delta S^0_{n-\mathrm{ioniz\,Be}_{(g)}} + \Delta S^0_{\mathrm{diss\,Be}^{n+}_{(g)}}.$$

The second includes the dissociation of molecular chlorine into atoms ($\Delta H^0_{\mathrm{diss\,Cl}_{2(g)}}$, $\Delta S^0_{\mathrm{diss\,Cl}_{2(g)}}$), the attachment of electrons to it ($\Delta H^0_{\mathrm{ioniz\,Cl}_{(g)}}$, $\Delta S^0_{\mathrm{ioniz\,Cl}_{(g)}}$), and the dissolution of gaseous chlorine ions in the melt ($\Delta H^0_{\mathrm{diss\,Cl}^{-}_{(g)}}$, $\Delta S^0_{\mathrm{diss\,Cl}^{-}_{(g)}}$). Here

$$\Delta H^0_{\mathrm{Cl}^{-}_{(melt)}} = \frac{1}{2}\Delta H^0_{\mathrm{diss\,Cl}_{2(g)}} + \Delta H^0_{\mathrm{ioniz\,Cl}_{(g)}} + \Delta H^0_{\mathrm{diss\,Cl}^{-}_{(g)}}$$

and

$$S^0_{\mathrm{Cl}^{-}_{(melt)}} = \frac{1}{2}\Delta S^0_{\mathrm{diss\,Cl}_{2(g)}} + \Delta S^0_{\mathrm{ioniz\,Cl}_{(g)}} + \Delta S^0_{\mathrm{diss\,Cl}^{-}_{(g)}} + \frac{1}{2}S^0_{\mathrm{Cl}_{2(g)}}.$$

The enthalpies and entropies of all the processes entering into these cycles, with one exception, have been measured and are known with a sufficient degree of accuracy. The only unknowns are the thermodynamic effects associated with the transfer of beryllium and chlorine ions from the gas phase into molten KCl. The purpose of the present work is to calculate them, proceeding from certain model concepts concerning the structure of molten KCl containing small amounts of dissolved beryllium chlorides, and concerning the nature of the interaction of its ionic components. These reduce to the following basic propositions:

1) In molten KCl there is preserved a short-range order in the mutual arrangement of cations and anions characteristic of the crystalline state. On melting, the number of Schottky vacancies increases by 20% (^{5}).

2) The work of removal of a chlorine anion and a potassium cation from KCl upon melting of the salt decreases in proportion to the increase in the number of vacancies.

3) The concentration of beryllium ions in the melt is sufficiently small, and their interaction with one another may be neglected.

4) Beryllium ions occupy cation vacancies; this is accompanied by distortions in the quasilattice of molten KCl: by attraction of chlorine anions around them and repulsion of ions of the same sign and of potassium cations. As a result, the bonds Be^{n+}—Cl^- prove to be stronger than K^+—Cl^-. Taking this interaction into account gives us the desired quantities $\Delta H^0_{\mathrm{Be}^{n+}(\mathrm{melt})}$ and $S^0_{\mathrm{Be}^{n+}(\mathrm{melt})}$.

5) A change in temperature, as experiments show ([3]), practically (within the limits of error of the e.m.f. measurements, down to 10^{-3} V) does not affect the enthalpies and entropies of the reactions taking place in galvanic cells with molten salt electrolytes.

If the potassium ion located at the point (000) of the quasilattice of molten KCl is replaced by a Be^{n+} ion, then the field created by this excess charge polarizes the other ions (charge polarization). In addition, owing to their different radii (K^+ and Be^{n+}), elastic displacements of ions occur (displacement polarization). Knowing these polarizations, one can determine the dipole moments of the polarized ions, and then the change in the total electrostatic potential at the point (000), due to all the dipoles of the medium:

$$\Delta\Phi = \frac{6e\xi}{a(1+\xi)} - \frac{6v}{a^2(1+\xi)^2} - \frac{qe}{a}\,(6.3346\,M_+ + 4.1977\,M_-), \tag{3}$$

where e is the unit charge; $qe = (n-1)e$ is the excess charge; ξ is the relative displacement of the anions of the first coordination sphere; a is the distance between anion and cation in KCl; v is the electric dipole moment of the nearest anions (for more detail see ([1],[2])). This expression was obtained as a result of summation over cations and anions, calculation of the component associated with the interaction of the nearest anions with the Be^{n+} cation (the first two terms), and neglect of the potential produced by the displacement of distant ions (because of the disordering of the quasilattice of the melt). The third term of the expression gives the potential due to charge polarization of the ions, beginning with the ions of the second coordination sphere.

In the zeroth approximation one may put $\xi = (r_{\mathrm{Be}^{n+}} - r_{\mathrm{K}^+})/a$; numerical calculation by equation (1) with $r_{\mathrm{Be}^+} = 0.56$, $r_{\mathrm{Be}^{2+}} = 0.34$, and $r_{\mathrm{K}^+} = 1.33$ Å gives $\Delta\Phi_{\mathrm{Be}^{2+}} \approx -5.7 \cdot 10^{-2}$ CGSE units and $\Delta\Phi_{\mathrm{Be}^+} = -2.9 \cdot 10^{-2}$ CGSE units.

Hence we obtain direct values for the change in enthalpy upon transfer of beryllium ions from the gas phase into the melt:

$$\Delta H^0_{\text{diss Be}^{2+}_{(\text{g})}} = \Delta H^0_{\text{diss K}^+} + 2e\Delta\Phi_{\text{Be}^{2+}} = -3.58 - 33.5 = -37.08 \text{ eV}$$

and

$$\Delta H^0_{\text{diss Be}^{+}_{(\text{g})}} = \Delta H^0_{\text{diss K}^+} + e\Delta\Phi_{\text{B}+} = -3.58 - 8.7 = -12.28 \text{ eV}.$$

Using literature data (^{4}) for the heat of sublimation $\Delta H^0_{\text{sub Be}_{(\text{s})}} = 3.255$ eV; for the ionization of Be to Be^+, $\Delta H'^0_{\text{ioniz Be}_{(\text{g})}} = 9.32$ eV, and to Be^{2+} ions, $\Delta H''^0_{\text{ioniz Be}_{(\text{g})}} = 27.53$ eV;

for the heat of dissociation of molecular chlorine $\Delta H^0_{\text{diss Cl}_{2(\text{g})}} = 2.475$ eV; the electron affinity of atomic chlorine $\Delta H^0_{\text{ioniz Cl}_{(\text{g})}} = 3.82$ eV, and the values found for the enthalpies of solution of the corresponding ions in molten KCl, we obtain for reaction (I) $\Delta H^0_{\text{calc}} = -141\,000$ cal/mol, while experimentally $\Delta H^0_{\text{exp}} = -54\,750$ cal/mol; for reaction (II) $\Delta H^0_{\text{calc}} = -442\,000$ cal/mol, while experimentally $\Delta H^0_{\text{exp}} = -122\,500$ cal/mol. The values of ΔH_{exp} are taken from work (^{3}), in which the authors, by the e.m.f. method, determined the thermodynamics of formation of beryllium mono- and dichloride in molten potassium chloride at sufficiently high dilutions. As can be seen, the discrepancies between the theoretical and experimental values are large. Apparently the reason for this is that in the calculation we simplified the picture and did not take into account the strongly polarizing action of the cation Be^{n+} on the surrounding chlorine anions. Obviously, in calculating the relative displacement ξ of the ions it is no longer possible to operate with crystallochemical values of ionic radii, since the latter will be strongly deformed. In this case the value ξ must be determined from the solution of the equation: $F_r + F_e = 0$, where F_r is the repulsive force, F_e the electrostatic attractive force between the cation Be^{n+} and the surrounding chlorine anions. Expressions for these forces are given in work (^{1}). Solution of the equation gives for Be^+ in molten KCl $\xi = -0.13$, whence $\Delta\Phi_{\text{Be}^+} = -1.4 \cdot 10^{-2}$ CGSE units, and consequently, in the new approximation, $\Delta H^0_{\text{soln Be}^+_{(\text{g})}} = -7.8$ eV, whence for reaction (I) we have

$$\Delta H^0_{\text{calc}} = -60\,000 \text{ cal/mol}.$$

For Be^{2+} we obtain $\xi = -0.155$, $\Delta\Phi_{\text{Be}^{2+}} = -3.5 \cdot 10^{-2}$ CGSE units, $\Delta H^0_{\text{soln Be}^{2+}_{(\text{g})}} = -24.5$ eV, and for reaction (II) we have

$$\Delta H^0_{\text{calc}} = 156\,000 \text{ cal/mol}.$$

Thus, we have obtained enthalpies that are considerably closer to the experimental ones than those obtained in the zero approximation. However, for Be^{2+}

the discrepancy is considerably greater than in the case of Be^{+}. This is probably due to the small dimensions of the Be^{2+} ion, as a result of which one should also take into account the interactions with one another of the chlorine anions drawn together around it.

In calculating the entropy of solution of Be^{n+} ions in molten KCl it was necessary to take into account the short-range order in the mutual arrangement of ions in the melt, namely, that in the sphere nearest to the cation there are anions, and the number of like beryllium cations in the subsequent cationic spheres increases with distance according to an exponential law. This can be written in the form of the following expression:

$$\Delta S^0_{\mathrm{soln\ Be}^{n+}_{(\mathrm{g})}} = kN \ln \left\{ [\mathrm{Be}^{n+}] \exp\left(-\frac{\varphi_j n_j e}{kT}\right) \exp\left(\frac{\varphi_i n_j e}{kT}\right) \times \right.$$

$$\left. \times \frac{(N+1)!}{(N+1-t)!\,t!} \cdot \frac{N!}{(N-t)!\,t!} \right\} - kN \ln \frac{N!}{(N-t)!\,t!} \cdot \frac{N!}{(N-t)!\,t!} - S^0_{\mathrm{Be}^{n+}_{(\mathrm{g})}}.$$

Here the factor $\exp(-\varphi_j n_j e/kT)$ expresses the probability of finding two Be^{n+} ions at a distance r from one another, $[\mathrm{Be}^{n+}]$ is their mole-fraction concentration in the melt, $\exp(\varphi_i n_j e/kT)$ is the probability of finding a chlorine anion in the immediate vicinity of the cation Be^{n+}; $n_j e$ is the charge of the ion; φ_i denotes the electrostatic potential of the form

$$\varphi_i = (n-1)e/a + 0.8(\Phi_1' + \Phi_2'),$$

where Φ_1' is the potential due to the charge polarization of the ions surrounding the Cl^{-} anion located in the first anionic sphere around the Be^{n+} cation; Φ_2' is the potential due to the polarization of displacement of the same ions; N is Avogadro' s number; t is the number of holes (anionic or cationic) per 1 mol of solvent salt; the second term of this expression is the entropy of the KCl melt.

Using the values we found for the entropies of solution of Be^{n+} and Cl^{-} ions in the melt, we obtain the entropies of the reactions of interest to us (I)

and (II) for the formation from the elements of beryllium mono- and dichloride in a KCl melt. For BeCl,

$$\Delta S^0_{\mathrm{diss}} = -15.46 + 4.6 \lg[\mathrm{Be}^{+}] \text{ cal/mol} \cdot \text{deg},$$

and for BeCl_2,

$$\Delta S^0_{\mathrm{diss}} = -44.89 + 4.6 \lg[\mathrm{Be}^{2+}] \text{ cal/mol} \cdot \text{deg}.$$

From the work $^{(3)}$ one can calculate the experimental values of these entropies at sufficiently low concentrations of beryllium in the melt. Thus, for example, for beryllium monochloride at $[\mathrm{Be}^{+}] = 10^{-4}$, $\Delta S^0_{\mathrm{diss}} = -33.86$ cal/mol • deg, whereas the value calculated from experimental data is $\Delta S^0_{\mathrm{exp}} = -29.93$ cal/mol • deg; for the dichloride at $[\mathrm{Be}^{2+}] = 10^{-2}$, $\Delta S^0_{\mathrm{diss}} = -54.19$ cal/mol • deg, whereas the value calculated from experimental data is $\Delta S^0_{\mathrm{exp}} = -39.76$ cal/mol • deg. At lower concentrations of beryllium ions, the agreement between calculated and experimental values is better. On the whole, the results of our calculations, within the possible errors of measurement and calculation, agree quite satisfactorily with one another.

Table 1

T, °K	$E^0_{\mathrm{Be/Be^+}}$ relative to chlorine electrode, V	$E^0_{\mathrm{Be/Be^+}}$ relative to chlorine electrode, V	$E_{\mathrm{Be/Be^{2+}}}$ relative to chlorine electrode, V	$E_{\mathrm{Be/Be^{2+}}}$ relative to chlorine electrode, V
T, °K	exp.	theor.	exp.	theor.
1100	−1.81	−1.85	−2.19	−2.31
1200	−1.77	−1.79	−2.14	−2.21
1300	−1.73	−1.72	−2.10	−2.12
1400	−1.67	−1.65	−2.10	−2.02

The calculated theoretical values of the enthalpies and entropies of reactions (I) and (II) make it possible to find expressions for the changes in Gibbs energy and for the apparent standard electrode potentials Be/Be^{+} and Be/Be^{2+} in molten KCl.

For the reaction

$$\mathrm{Be}_{(\mathrm{s})} + \tfrac{1}{2}\mathrm{Cl}_{2(\mathrm{g})} = \mathrm{BeCl}_{(\mathrm{melt})}:$$

$$\Delta\mathcal{G}_1 = -60000 + 15.5T \text{ cal/mol},$$

$$E^0_{\mathrm{Be/Be^+}} = \Delta\mathcal{G}_1/23062 = -2.60 + 6.8 \cdot 10^{-4}T.$$

For the reaction

$$\mathrm{Be}_{(\mathrm{s})} + \mathrm{Cl}_{2(\mathrm{g})} = \mathrm{BeCl}_{2(\mathrm{melt})}:$$

$$\Delta\mathcal{G}_2 = -156000 + 44.9T \text{ cal/mol},$$

$$E^0_{\mathrm{Be/Be^{2+}}} = \frac{\Delta\mathcal{G}_2}{46124} = -3.38 + 9.73 \cdot 10^{-4} T.$$

In Table 1 the experimental values (3) are compared with those calculated from the theoretical equations derived by us.

The calculation for univalent beryllium gives agreement with experiment within 5% (in the present temperature interval); in the case of divalent beryllium the discrepancies reach 15%. This indicates that, in the case of a strongly polarizing cation, the interaction with the salt solvent must be treated in still greater detail.

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Note: Figure translations are in progress. See original paper for figures.