Die schon im Ionisierungsraum durch den Zerfall des SF_6^- gebildeten Ionen müssen im Spektrum bei ihrer eigenen Masse m_1 auftreten. Sie sind auch praktisch immer bei 0 eV Elektronenenergie, d. h. energetisch ebenso wie das Ausgangsion SF_6^- beobachtet worden. Das Gleiche gilt natürlich entsprechend für den Zerfall des SF_5^--Ions.

Tabelle 2 gibt eine Übersicht über die beobachteten metastabilen Peaks und ihre so gefunden Deutung.

Effektive Masse	Energieabhängigkeit entsprechend	angenommener Zerfall
2,4	SF_6^-	$SF_6^- \rightarrow F^- + R$
2,7	SF_5^-	$SF_5^- \rightarrow F^- + R$
9,5	SF_6^-	$SF_6^- \rightarrow F_2^- + R$
18,7	SF_6^-	$SF_6^- \rightarrow SF^- + R$
37,5	SF_6^-	$SF_6^- \rightarrow SF_2^- + R$
54,5	SF_6^-	$SF_6^- \rightarrow SF_3^- + R$
80,0	SF_6^-	$SF_6^- \rightarrow SF_4^- + R$
91	SF_5^-	$SF_5^- \rightarrow SF_4^- + R$
(110	SF_6^-	$SF_6^- \rightarrow SF_5^- + R)$

Tab. 2. Übersicht über die metastabilen Peaks der Abb. 2.

Es fällt auf, daß anscheinend ein S^--Ion weder primär (bei 20 – 24 eV vermutet) noch als Zerfallsprodukt auftritt und ein SF^--Ion ebenfalls nicht über dissoziativen Resonanzeinfang, wohl aber über den Zerfall des SF_6^-.

Durch die endliche Breite des Trennrohraustrittsspaltes können Ionen, die im letzten Teil des Magnetfeldes autoionisieren, trotz ihrer dann gradlinigen Bahn noch das Trennrohr verlassen und am SEV einen Impuls auslösen. Diese Autoionisation führt dann im Massenspektrum zu dem auch beobachteten schwächeren Abfall des Peaks zu höheren Massen hin. Die gleiche Beobachtung am Peak des SF_5^- scheint auf eine Autoionisation auch dieses Ions hinzudeuten.

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Centrifugal and Gravitational Cells Containing Molten Salts with Three Ion Constituents

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Since recently[1] the first experimental data on centrifugal and gravitational cells containing molten salts have been published, the rigorous derivation of the formulae for the EMF of this type of galvanic cells will now be given.

The corresponding formulae for aqueous electrolyte solutions have been obtained by MILLER[2] and independently by SCHÖNERT[3] who also included polyelectrolyte solutions. Both authors refer to experimental investigations of TOLMAN[4], GRINNEL and KOENIG[5], MACINNES, RAY, and coworkers[6–8], who proved that the measurements of the EMF of centrifugal cells represent a precision method for the determination of transport numbers in electrolyte solutions.

If we restrict the discussion to isothermal cells we may indicate a centrifugal or gravitational cell in the following form

		a		b		c		d		
	Terminal (A)		Electrode (B)		Molten Salt		Electrode (B)		Terminal (A)	
Pressure:	P		P		P		$P+\Delta P$		$P+\Delta P$	P
Height:	h		h		h		$h+\Delta h$		$h+\Delta h$	h

We obtain the general formula for the EMF of this cell from Thermodynamics of Irreversible Processes[9]:

$$F\,\Phi = \int_P^{P+\Delta P}\left[\frac{M_\Theta}{\varrho_A} - \frac{V_a}{z_r} + \frac{V_r}{z_r}\right]\mathrm{d}P + \int_P^{P+\Delta P}\sum_k \frac{\vartheta_k}{z_k}\left(\frac{M_k}{\varrho} - V_k\right)\mathrm{d}P$$
$$-\int_b^c \sum_k \frac{\vartheta_k}{z_k}\,(\mathrm{d}\mu_k)_{T,P} + \frac{1}{z_r}\int_b^c (\mathrm{d}\mu_r)_{T,P}\,, \tag{1}$$

where F denotes the Faraday constant, Φ the EMF, P the pressure, M_Θ and M_k the molar mass of the electron and of ion constituent k respectively, V_a, V_r and V_k the partial molar volume of a (species a is the neutral atomic species belonging to r), of r (r is the ionic species for which the electrodes are reversible), and of k respectively; ϱ_A and ϱ denote the density of the terminal A and the molten salt respectively, z_k the charge number, ϑ_k the stoichiometric transport number and μ_k the chemical potential of ion constituent k.

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Equation (1) is valid for any number of ion constituents. We have introduced the stoichiometric transport numbers ϑ_k here since the reduced transport numbers occuring in the original formula [9] are inappropriate for the description of ionic melts. For the ion constituent chosen as reference system we have: $\vartheta_k \equiv 0$. Thus the summations in Eq. (1) may be formally extended over all ion constituents.

Comparing Eq. (1) to the equations derived previously [10], we see that the last two integrals in Eq. (1), which are to be taken over a range of concentrations at constant pressure, represent the term for the EMF of a concentration cell with transference. For $\Delta P \to 0$ and $\Delta h \to 0$ the centrifugal or gravitational cell becomes a pure concentration cell. Thus the two first integrals in Eq. (1) represent the initial value of the EMF.

In the following we consider a mixture of two molten salts containing three ion constituents altogether (example: $AgNO_3 + Ba(NO_3)_2$, the electrodes being silver electrodes, for example]. We designate the two salts as components 1 and 2 ($i=1, 2$). The ion constituent occurring in component 1 only will be denote by α, the ion constituent occurring in component 2 only will be denote by β, and the ion constituent common to both components by γ ($k=\alpha, \beta, \gamma$). We consider the average velocity $\boldsymbol{v}_\gamma$ of the common ions as reference velocity $\boldsymbol{w}$. We also suppose that the electrodes are reversible to α ($r=\alpha$). We then obtain, using the condition of electrical neutrality as well as the relations

$$\frac{M_\alpha}{z_\alpha} - \frac{M_\gamma}{z_\gamma} = \frac{M_1}{z_\alpha \nu_\alpha} = -\frac{M_1}{z_\gamma \nu_\gamma}; \qquad \frac{M_\beta}{z_\beta} - \frac{M_\gamma}{z_\gamma} = \frac{M_2}{z_\beta \nu_\beta} = -\frac{M_2}{z_\gamma \nu_\gamma};$$

$$\frac{V_\alpha}{z_\alpha} - \frac{V_\gamma}{z_\gamma} = \frac{V_1}{z_\alpha \nu_\alpha} = -\frac{V_1}{z_\gamma \nu_\gamma}; \qquad \frac{V_\beta}{z_\beta} - \frac{V_\gamma}{z_\gamma} = \frac{V_2}{z_\beta \nu_\beta} = -\frac{V_2}{z_\gamma \nu_\gamma}$$

the following formula for the initial value of the EMF

$$F\,\Phi_0 = \int_P^{P+\Delta P} \left\{ \frac{M_\Theta}{\varrho \mathrm{A}} - \frac{V_\mathrm{a}}{z_\alpha} + \frac{M_\alpha}{z_\alpha\,\varrho} - \frac{1-{}_\gamma\vartheta_\alpha}{z_\gamma \nu_\gamma} \left[\frac{M_2 - M_1}{\varrho} - (V_2 - V_1) \right] \right\} \mathrm{d}P. \quad (r=\alpha,\ \boldsymbol{w}=\boldsymbol{v}_\gamma). \tag{2}$$

Here ${}_\gamma\vartheta_\alpha$ is the stoichiometric transport number of α with reference to γ. Adding up the term for the EMF of the concentration cell, we find:

$$F\,\Phi = F\Phi_0 + \frac{1}{z_\gamma \nu_\gamma} \int_b^c (1 - {}_\gamma\vartheta_\alpha)\,(\mathrm{d}\mu_2 - \mathrm{d}\mu_1) \qquad (r=\alpha,\ \boldsymbol{w}=\boldsymbol{v}_\gamma). \tag{3}$$

In the case of sedimentation equilibrium we find the final value of the EMF of the centrifugal cell. In another paper [11] we proved that the condition for sedimentation equilibrium

$$(M_i - \varrho\,V_i)\ \boldsymbol{g} = (\mathrm{grad}\,\mu_i)_{T,P} \quad (i=1,2)$$

holds without any restriction for the *neutral* components of a molten salts without a fixed phase (porous glas disc, sinter plate). $\boldsymbol{g}$ denotes the gravitational acceleration. For the one-dimensional case we obtain with $\varrho\,\boldsymbol{g} = \mathrm{grad}\,P$ the final value of the EMF:

$$F\,\Phi_\infty = \int_P^{P+\Delta P} \left(\frac{M_\Theta}{\varrho \mathrm{A}} - \frac{V_\mathrm{a}}{z_\alpha} + \frac{M_\alpha}{z_\alpha\,\varrho} \right) \mathrm{d}P, \qquad (r=\alpha,\ \boldsymbol{w}=\boldsymbol{v}_\gamma). \tag{4}$$

If we calculate the transport numbers, we have to determine them from the difference

$$F(\Phi_\infty - \Phi_0) = \frac{1}{z_\gamma \nu_\gamma} \int_P^{P+\Delta P} (1 - {}_\gamma\vartheta_\alpha) \left[\frac{M_2 - M_1}{\varrho} - (V_2 - V_1) \right] \mathrm{d}P, \quad r=\alpha,\ \boldsymbol{w}=\boldsymbol{v}_\gamma). \tag{5}$$

The corresponding equations of the gravitational cell follow from the condition of mechanical equilibrium $\mathrm{d}P = -\varrho\,g\,\mathrm{d}h$.

$$F\,\Phi_0 = \int_h^{h+\Delta h} \left\{ \frac{V_\mathrm{a}\,\varrho}{z_\alpha} - \frac{M_\Theta\,\varrho}{\varrho \mathrm{A}} - \frac{M_\alpha}{z_\alpha} - \frac{1-{}_\gamma\vartheta_\alpha}{z_\gamma \nu_\gamma} \left[M_2 - M_1 - \varrho(V_2 - V_1) \right] \right\} g\,\mathrm{d}h, \qquad (r=\alpha,\ \boldsymbol{w}=\boldsymbol{v}_\gamma), \tag{6}$$

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$$F\,\Phi_\infty = \int\limits_h^{h+\Delta h} \left(\frac{V_a\,\varrho}{z_\alpha} - \frac{M_\Theta\,\varrho}{\varrho_A} - \frac{M_\alpha}{z_\alpha} \right) g\,\mathrm{d}h \qquad (r=\alpha,\ \boldsymbol{w}=\boldsymbol{v}_\gamma) \tag{7}$$

and the difference of these two equations.

In the same reference frame ($\boldsymbol{w}=\boldsymbol{v}_\gamma$) the electrodes can also be reversible for the ionic species β ($r=\beta$). We then obtain the initial value of the EMF

$$F\,\Phi_0 = \int\limits_P^{P+\Delta P} \left\{ \frac{M_\Theta}{\varrho_A} - \frac{V_a}{z_\beta} + \frac{M_\beta}{z_1\,\varrho} + \frac{1-{}_\gamma\vartheta_\beta}{z_\gamma\,\nu_\gamma} \left[\frac{M_2-M_1}{\varrho} - (V_2-V_1) \right] \right\} \mathrm{d}P \qquad (r=\beta,\ \boldsymbol{w}=\boldsymbol{v}_\gamma) \tag{8}$$

and the final value

$$F\,\Phi_\infty = \int\limits_P^{P+\Delta P} \left(\frac{M_\beta}{z_\beta\,\varrho} - \frac{V_a}{z_\beta} + \frac{M_\Theta}{\varrho_A} \right) \mathrm{d}P\,, \quad (r=\beta,\ \boldsymbol{w}=\boldsymbol{v}_\gamma). \tag{9}$$

Finally we must deal with the case $r=\gamma$, $\boldsymbol{w}=\boldsymbol{v}_\gamma$:

$$F\,\Phi_0 = \int\limits_P^{P+\Delta P} \left\{ \frac{M_\Theta}{\varrho_A} - \frac{V_a}{z_\gamma} + \frac{M_\gamma}{z_\gamma\,\varrho} - \frac{1}{z_\gamma\,\nu_\gamma} \left(\frac{M_1}{\varrho} - V_1 \right) - \frac{{}_\gamma\vartheta_\beta}{z_\gamma\,\nu_\gamma} \left[\frac{M_2-M_1}{\varrho} - (V_2-V_1) \right] \right\} \mathrm{d}P\,, \quad (r=\gamma,\ \boldsymbol{w}=\boldsymbol{v}_\gamma). \tag{10}$$

We see that Eq. (10) has a form slightly different from Eq. (2) or (8) with regard to ${}_\gamma\vartheta_\gamma \equiv 0$. Φ_∞, however, remains analogous

$$F\,\Phi_\infty = \int\limits_P^{P+\Delta P} \left(\frac{M_\Theta}{\varrho_A} - \frac{V_a}{z_\gamma} + \frac{M_\gamma}{z_\gamma\,\varrho} \right) \mathrm{d}P\,, \quad (r=\gamma,\ \boldsymbol{w}=\boldsymbol{v}_\gamma). \tag{11}$$

Because of the sedimentation equilibrium, Eqs. (4), (9) and (11) describe a reversible cell and they can represented by a common equation

$$F\,\Phi_\infty = \int\limits_P^{P+\Delta P} \left(\frac{M_\Theta}{\varrho_A} - \frac{V_a}{z_r} + \frac{M_r}{z_r\,\varrho} \right) \mathrm{d}P \qquad (r=\alpha,\beta,\gamma). \tag{12}$$

Equation (12) is also correct without any change in the other possible reference frames, because there is no quantity in it depending of the reference frame. Equation (12) is also identical with the formula of the EMF of the reversible centrifugal cell containing only one pure molten salt.

The formulae for Φ_0 cannot be represented in such a closed form, because all contain one independent transport number, which depends on the reference frame. In the following we give the formulae for Φ_0 in the reference frame $\boldsymbol{w}=\boldsymbol{v}_\alpha$ and $\boldsymbol{w}=\boldsymbol{v}_\beta$:

$$F\,\Phi_0 = \int\limits_P^{P+\Delta P} \left[\frac{M_\Theta}{\varrho_A} - \frac{V_a}{z_\alpha} + \frac{M_\alpha}{z_\alpha\,\varrho} + \frac{1}{z_\gamma\,\nu_\gamma} \left(\frac{M_1}{\varrho} - V_1 \right) - \frac{{}_\alpha\vartheta_\beta}{z_\gamma\,\nu_\gamma} \left(\frac{M_2}{\varrho} - V_2 \right) \right] \mathrm{d}P\,, \quad (r=\alpha,\ \boldsymbol{w}=\boldsymbol{v}_\alpha), \tag{13}$$

$$F\,\Phi_0 = \int\limits_P^{P+\Delta P} \left[\frac{M_\Theta}{\varrho_A} - \frac{V_a}{z_\beta} + \frac{M_\beta}{z_\beta\,\varrho} + \frac{1-{}_\alpha\vartheta_\beta}{z_\gamma\,\nu_\gamma} \left(\frac{M_2}{\varrho} - V_2 \right) \right] \mathrm{d}P\,, \quad (r=\beta,\ \boldsymbol{w}=\boldsymbol{v}_\alpha), \tag{14}$$

$$F\,\Phi_0 = \int\limits_P^{P+\Delta P} \left[\frac{M_\Theta}{\varrho_A} - \frac{V_a}{z_\gamma} + \frac{M_\gamma}{z_\gamma\,\varrho} - \frac{1-{}_\alpha\vartheta_\gamma}{z_\gamma\,\nu_\gamma} \left(\frac{M_2}{\varrho} - V_2 \right] \mathrm{d}P\,, \quad (r=\gamma,\ \boldsymbol{w}=\boldsymbol{v}_\alpha), \tag{15}$$

$$F\,\Phi_0 = \int\limits_P^{P+\Delta P} \left[\frac{M_\Theta}{\varrho_A} - \frac{V_a}{z_\alpha} + \frac{M_\alpha}{z_\alpha\,\varrho} + \frac{1-{}_\beta\vartheta_\alpha}{z_\gamma\,\nu_\gamma} \left(\frac{M_1}{\varrho} - V_1 \right) \right] \mathrm{d}P\,, \quad (r=\alpha,\ \boldsymbol{w}=\boldsymbol{v}_\beta), \tag{16}$$

$$F\,\Phi_0 = \int\limits_P^{P+\Delta P} \left[\frac{M_\Theta}{\varrho_A} - \frac{V_a}{z_\beta} + \frac{M_\beta}{z_\gamma\,\varrho} + \frac{1}{z_\gamma\,\nu_\gamma} \left(\frac{M_2}{\varrho} - V_2 \right) - \frac{{}_\beta\vartheta_\alpha}{z_\gamma\,\nu_\gamma} \frac{M_1}{\varrho} - V_1 \right) \right] \mathrm{d}P\,, \quad (r=\beta,\ \boldsymbol{w}=\boldsymbol{v}_\beta), \tag{17}$$

$$F\,\Phi_0 = \int\limits_P^{P+\Delta P} \left[\frac{M_\Theta}{\varrho_A} - \frac{V_a}{z_\gamma} + \frac{M_\gamma}{z_\gamma\,\varrho} - \frac{1-{}_\beta\vartheta_\gamma}{z_\gamma\,\nu_\gamma} \left(\frac{M_1}{\varrho} - V_1 \right) \right] \mathrm{d}P\,, \quad (r=\gamma,\ \boldsymbol{w}=\boldsymbol{v}_\beta). \tag{18}$$

We easily obtain the corresponding equations for gravitational cells in the manner indicated above.

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