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Thermogalvanic Cells with a Single Fused Salt

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This paper reviews the theory of thermogalvanic cells with metal or halogen electrodes and a single fused salt, and analyses the results of experimental studies of thermogalvanic cells (including those obtained in the author's laboratory). Some examples of the application of thermopotentials in studies of the physical chemistry of fused salts are discussed. 47 references.

CONTENTS

1. Introduction 250
2. Model of the thermogalvanic cell, and location of the thermopotential 251
3. Relation between the thermopotential and the temperature coefficient of the e.m.f. of the isothermal chemical cell 251
4. Thermopotential equation 252
5. Heterogeneous component of the thermopotential 252
6. Entropy of transfer in the salt 253
7. Dependence of the thermopotential and its components upon the state of aggregation of the electrodes and the electrolyte 254
8. Applications of the thermopotential 255

1. INTRODUCTION

Two identical reversible electrodes held at different temperatures and connected by a fused electrolyte containing the potential-determining ions will generate a thermo-e.m.f whose magnitude depends first and foremost on the temperature difference and on the nature of the element. A thermogalvanic element of this type is usually characterised by the temperature coefficient of its thermo-e.m.f., for which we shall use the term "thermopotential". Equivalent terms often used in the literature include "thermo-electric power" and "Seebeck coefficient". When a cell of this type is short-circuited, current flows in a direction such that the electrode reaction at the hotter electrode is continuously absorbing heat, and vice-versa. Hence, the only driving force for the generation of electrical energy is the transfer of heat from the hotter to the cooler region.

The study of thermoelectric phenomena in fused salts includes a wide range of problems of great theoretical and practical importance. During the past decades, a great deal of work has been done on non-isothermal fused electrolyte systems because of the possibility of finding useful applications in the field of thermo-electricity and also in order to increase our understanding of the transfer of heat and electricity in ionic melts. Studies of thermogalvanic cells enable us to characterise the electrode reaction at the electrode–fused salt interface and give some insight into the structure of ionic melts. Enough experimental information on thermogalvanic cells with a single fused salt is available for a general analysis of the thermoelectric effect and its components as a function of the nature and the state of aggregation of the electrodes and the electrolyte. The thermogalvanic cells with a single fused salt which have been studied up to the present are listed in Table 1.

Table 1. Thermogalvanic cells with a single fused salt.

Thermogalvanic cell	Temp., °C	Thermopotential, mV deg^{-1}	Ref.
Graphite, Cl_2 | LiCl | Cl_2, graphite	700—1100	—0.540	1
	650—850	—0.534	2
Graphite, Cl_2 | NaCl | Cl_2, graphite	820—990	—0.45	3
	900—1300	—0.48 ÷ —0.415	1
	850	—0.483	3
Graphite, Cl_2 | KCl | Cl_2, graphite	850—1200	—0.475 ÷ —0.420	1
	800	—0.504	2
	830	—0.40	3
Graphite, Cl_2 | RbCl | Cl_2, graphite	750	—0.544	2
Graphite, Cl_2 | CsCl | Cl_2, graphite	700	—0.533	2
Cu | CuCl | Cu	462—588	—0.436	4
	450—590	—0.42	5
Cu | CuBr | Cu	620	—0.47	6
	500—700	—0.48	5
Cu | CuI | Cu	610—710	—0.510	6
	610—700	—0.53	5
Ag | AgF | Ag	435—550	—0.38	5
	500—900	—0.664	7
	500—900	—0.665	1
Graphite, Cl_2 | AgCl | Cl_2, graphite	430—680	—0.667	2
	470—645	—0.695	8
Ag | AgCl | Ag	455—650	—0.41	9
	490—590	—0.42	10
	500—900	—0.375	7
	470—570	—0.400	8
	500—625	—0.404 ÷ —0.396	11
	455—570	—0.44	5
Graphite, Br_2 | AgBr | Br_2, graphite	480—670	—0.701 ÷ 0.633	12
Ag | AgBr | Ag	450—550	—0.456	10
	450—600	—0.440	13
	450—550	—0,6	5
Ag | AgI | Ag	564—624	—0.498	10
	560—650	—0.490	6
	560—600	—0.52	5
Ag | $AgNO_3$ | Ag	230—375	—0.344	15
	210—310	—0.33	3
	239—311	—0.306	16
	215—347	—0.322 ÷ —0.331	14

Table 1 contd.

Thermogalvanic cell	Temp., °C	Thermopotential, mV deg^{-1}	Ref.
Ag | Ag_2SO_4 | Ag	657—750	—0.310	17
Graphite Cl_2 | $ZnCl_2$ | Cl_2, graphite	440—600	—0.65 ÷ —0.73	18
$Zn_{sol.}$ | $ZnCl_2$ | $Zn_{sol.(liq.)}$	347—580	+0.053 ÷ —0.035	18
$Zn_{liq.}$ | $ZnCl_2$ | $Zn_{liq.}$	450—600	+0.05 ÷ —0.03	18
	428—550	+0.032 ÷ —0.02	20
$Zn_{liq.}$ | $ZnBr_2$ | $Zn_{liq.}$	420—600	—0.05	19, 21
	428—548	—0.04	20
$Zn_{liq.}$ | ZnI_2 | $Zn_{liq.}$	439—530	—0.119 ÷ —0.094	20
Graphite Cl_2 | $CdCl_2$ | Cl_2, graphite	580—720	—0.714	22
$Cd_{liq.}$ | $CdCl_2$ | $Cd_{liq.}$	580—720	—0.146	23
$Cd_{liq.}$ | $CdBr_2$ | $Cd_{liq.}$	620—720	—0.135	23
$Cd_{liq.}$ | CdI_2 | $Cd_{liq.}$	400—600	—0.118	23
$Sn_{liq.}$ | $SnCl_2$ | $Sn_{liq.}$	263—463	—0.03 ÷ —0.04	22
	230—520	—0.014	20
$Sn_{liq.}$ | $SnBr_2$ | $Sn_{liq.}$	244—440	+0.04	20
$Sn_{liq.}$ | SnI_2 | $Sn_{liq.}$	339—455	—0.05 ÷ —0.04	20
	550	—0.587	2
Graphite Cl_2 | $PbCl_2$ | Cl_2, graphite	530—630	—0.620	24
	525—675	—0.006	3
$Pb_{liq.}$ | $PbCl_2$ | $Pb_{liq.}$	530—630	—0.008	24
	519—650	—0.013	20
$Pb_{liq.}$ | $PbBr_2$ | $Pb_{liq.}$	420—680	—0.037 ÷ —0.041	3
	421—506	—0.02	20
$Pb_{liq.}$ | PbI_2 | $Pb_{liq.}$	438—478	+0.04	20

2. MODEL OF THE THERMOGALVANIC CELL AND LOCATION OF THE THERMOPOTENTIAL

The location of the thermopotential in a thermogalvanic cell consisting of two identical, reversible solid electrodes can be described by the model shown in Fig. 1. (The two electrodes are immersed in the same fused salt, containing ions of this metal in a single state of oxidation.) If T_2 and T_1 differ by 1°, the thermo-e.m.f. measured between the electrodes is equal to the thermopotential of the cell. The thermopotential is the algebraic sum of five quantities: the potential steps (having opposite signs) at the electrode—melt interfaces at temperatures T_2 and T_1, the potential differences in the metallic conductors due to the temperature differences $(T_2 - T_0)$ and $(T_1 - T_0)$, also having opposite signs, and the potential difference due to the temperature difference within the electrolyte.

To simplify the theoretical analysis of the thermopotential, we shall assume a temperature distribution within the cell as shown in Fig. 1: each electrode will be treated as if it were in an isothermal region. Our experiments were designed to produce a temperature distribution of this type. A thermogalvanic cell consisting of two halogen electrodes on an indifferent carrier (for example, graphite) and a suitable salt can be represented by an analogous model.

In the case of a thermogalvanic cell with two liquid metal electrodes (M_I) to which contact is made with solid electronic conductors (M_{II}), a correction must be made to the measured thermopotential for the thermopotential of the couple M_I/M_{II}. The potential gradient in the liquid metal is ignored because it is much smaller than the thermopotential for a temperature difference of the order of one degree.

3. RELATION BETWEEN THE THERMOPOTENTIAL AND THE TEMPERATURE COEFFICIENT OF THE E.M.F. OF THE ISOTHERMAL CHEMICAL CELL

Reinhold[25], in his work on thermogalvanic cells with solid electrolytes, first pointed out that the measured thermopotentials can conveniently be tested against the temperature coefficient of the appropriate isothermal chemical cell. The relationship between these quantities can easily be derived analytically[8], and it also follows from the diagram of Fig. 2.

Adding all the e.m.f.'s in this circuit, and equating to zero, we obtain the following expression:

$$\left(\frac{dE}{dT}\right)_{X_2} - \left(\frac{dE}{dT}\right)_{M} = \left(\frac{dE}{dT}\right)_{chem} - \left(\frac{dE}{dT}\right)_{M-C}. \quad (1)$$

The thermopotentials $(dE/dT)_{X_2}$ and $(dE/dT)_M$ are given a sign corresponding to the polarity of the "hot" electrode, and the thermopotential of the pair M—C is given a sign corresponding to the polarity of the metal with respect to graphite. We shall consider a few examples of the application of Eqn. (1).

For the thermogalvanic cell $Ag_{T_2}|AgCl_{melt}|_{T_1}Ag$ we have the following thermopotential: $(dE/dT)_{Ag} = -0.400 \times 10^{-3}$ V deg^{-1}; for the cell $Cl_2{}_{T_2}|AgCl_{melt}|_{T_1}Cl_2$ we have $(dE/dT)_{Cl_2} = -0.695 \times 10^{-3}$ V deg^{-1}; for the

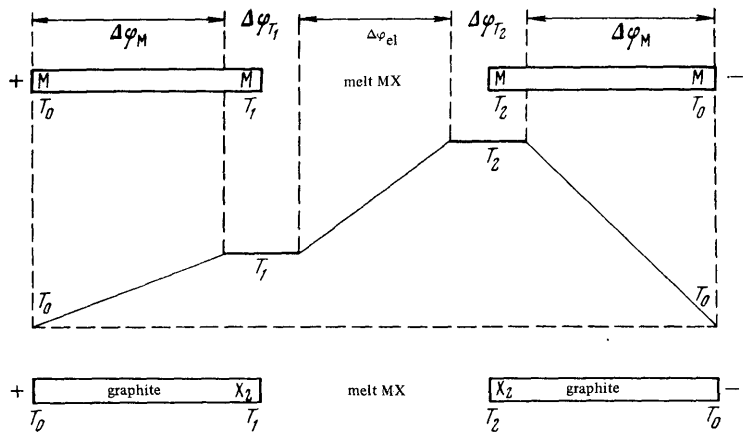


Figure 1. Model of a thermogalvanic cell and location of the thermopotential.

Ag—C thermocouple we have $(dE/dT)_{Ag-C} = +1 \times 10^{-6}$ V deg^{-1}.[8] Inserting these values into Eqn. (1) we obtain $(dE/dT)_{chem.\ calc.} = -0.285 \times 10^{-3}$ V deg^{-1}. The most reliable measurements of the e.m.f. of the chemical cell $Ag|AgCl_{melt}|Cl_2$, reported by different workers, lead to the following values for the temperature coefficient of the e.m.f.: 0.292×10^{-3} V deg^{-1},[26] 0.289×10^{-3} V deg^{-1},[27] and 0.294×10^{-3} V deg^{-1}.[8] Thus, the agreement between the measured temperature coefficient and the value calculated from the thermopotentials is within experimental error.

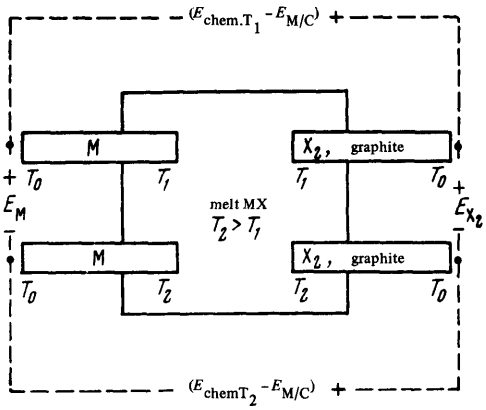


Figure 2. Relationship between the e.m.f.'s of the thermogalvanic cells and the e.m.f. of the isothermal chemical cell with a single fused salt.

The experimentally measured thermopotential for the thermogalvanic cell $Pb_{liq.}\,T_2|PbCl_2 melt|T_1\,Pb_{liq.}$ is $(dE/dT)_{Pb} = -0.008 \times 10^{-3}$ V deg^{-1}, for the cell $Cl_2T_2|PbCl_2 melt|T_1Cl_2$ we find $(dE/dT)_{Cl_2} = -0.620 \times 10^{-3}$ V deg^{-1}, and for the Pb—C couple $(dE/dT)_{Pb-C} = +0.001 \times 10^{-3}$ V deg^{-1}.[24] From Eqn. (1) we obtain $(dE/dT)_{chem.\ calc.} = -0.61 \times 10^{-3}$ V deg^{-1}. Direct measurements of the e.m.f. of the chemical cell $Pb|PbCl_2 melt|Cl_2$ gave the following values of the temperature coefficient: -0.60×10^{-3} V deg^{-1} [28] and -0.62×10^{-3} V deg^{-1}.[29]

For the thermogalvanic cell $Cd_{liq.}\,T_2|CdCl_2 melt|T_1\,Cd_{liq.}$ we find $(dE/dT)_{Cd} = -0.146 \times 10^{-3}$ V deg^{-1}; for the cell $Cl_2T_2|CdCl_2 melt|T_1Cl_2$, $(dE/dT)_{Cl_2} = -0.714 \times 10^{-3}$ V deg^{-1}; for the $Cd_{liq.}$—C couple, $(dE/dT)_{Cd-C} = -0.0075 \times 10^{-3}$ V deg^{-1}.[22] Hence $(dE/dT)_{chem.\ calc.} = -0.575 \times 10^{-3}$ V deg^{-1}, whereas the experimentally measured value[30] is -0.568×10^{-3} V deg^{-1}. For fused zinc chloride[18] the thermopotential difference[30] is -0.700×10^{-3} V deg^{-1}; the thermopotential of the $Zn_{liq.}$—C couple is $+0.005 \times 10^{-3}$ V deg^{-1}. Hence $(dE/dT)_{chem.\ calc.} = -0.695 \times 10^{-3}$ V deg^{-1}. From the measured e.m.f.'s of the cell $Zn_{liq.}|ZnCl_2 melt|Cl_2$, the temperature coefficient is given as -0.695×10^{-3} V deg^{-1},[29] -0.697×10^{-3} V deg^{-1},[31] and -0.700×10^{-3} V deg^{-1}.[32] The agreement between calculation and experiment is good.

4. THERMOPOTENTIAL EQUATION

We shall derive an equation for the thermopotential by considering the components of this potential, as shown in Fig. 1.

According to Wagner[33], the thermopotential can be divided into two components: a heterogeneous thermoelectric effect, arising from the electrochemical reaction at the electrode—electrolyte boundary, and a homogeneous thermoelectric effect, due to the temperature gradient in the electrolyte and in the electrodes.

For the thermogalvanic cell $M_{T+dT}|MX_{melt}|T^M$, the heterogeneous thermoelectric effect $(dE/dT)_M^{het}$ can be expressed as the difference between the potential steps at the electrode—electrolyte interface: $(dE/dT)_M^{het} = \Delta\varphi_{T+dT} - \Delta\varphi_T$. The passage of one Faraday of electricity through the electrode—electrolyte interface alters the free energy of the system, as a result of the reaction $M \rightarrow M^+ + e$, by an amount $\Delta G = F \cdot \Delta\varphi$. Hence, for the whole cell, $F \cdot (dE/dT)_M^{het} = \Delta G_{T+dT} - \Delta G_T = -\Delta S$, where ΔS is the entropy change attending the reaction. Expressing ΔS as the difference $\Delta S = \bar{S}_{M^+} + \bar{S}_e^M - S_M$, we obtain

$$F \cdot \left(\frac{dE}{dT}\right)_M^{het} = S_M - \bar{S}_{M+} - \bar{S}_e^M \qquad (2)$$

where S_M is the absolute entropy of the metal at temperature T, $\bar{S}_{M^+}$ is the partial entropy of the M^+ ion in the electrolyte, and $\bar{S}_e^M$ is the partial entropy of an electron in the metal.

The homogeneous thermoelectric effect, as a component of the thermopotential, can itself be expressed as the resultant of two effects: one due to the temperature gradient in the electrolyte and one due to the temperature gradient in the metal:

$$F \cdot \left(\frac{dE}{dT}\right)_M^{hom} = \overset{*}{S}_i - \overset{*}{S}_e^M \qquad (3)$$

where $\overset{*}{S}_i$ is the entropy of transfer in the electrolyte, $\overset{*}{S}_e^M$ is the entropy of transfer of an electron in the metal. By adding Eqns. (2) and (3) we obtain the equation for the thermopotential of a thermogalvanic cell with metallic electrodes:

$$F \cdot \left(\frac{dE}{dT}\right)_M = S_M - \bar{S}_{M+} + \overset{*}{S}_i - (\bar{S}_e + \overset{*}{S}_e)^M \quad . \qquad (4)$$

Similarly, for a thermogalvanic cell with halogen electrodes we obtain

$$F\left(\frac{dE}{dT}\right)_{X_2} = \bar{S}_{X^-} - \frac{1}{2}S_{X_2} + \overset{*}{S}_i - (\bar{S}_e + \overset{*}{S}_e)^c \qquad (4')$$

where S_{X_2} is the absolute entropy of the halogen, $\bar{S}_{X^-}$ is the partial entropy of the halide ion. Thermopotential equations have been derived also from irreversible thermodynamics[34,35].

5. HETEROGENEOUS COMPONENT OF THE THERMOPOTENTIAL

In the calculation of the heterogeneous component of the thermopotential of a thermogalvanic cell with metallic electrodes the partial entropy of electrons in the metal [Eqn. (2)] is much smaller than the other components and can be ignored[36].

The absolute entropy S_M of the metal at the temperature T for which the thermopotential is measured can be found in standard thermodynamic tabulations[37,38]. The difficulty arises in computing the partial entropy of the ion. In 1929 Wagner had suggested taking the partial entropy of an ion in a uni-univalent electrolyte as one-half of the entropy of the salt[33]. A more valid method, put forward by Pitzer[39], takes into account the mass (M) of both the cation and the anion: Pitzer's equation is

$$\bar{S}_{M+} = \frac{1}{2}\left(S_{MX} + \frac{3}{2} R \ln \frac{M_M}{M_X}\right) \quad (5)$$

Eqn. (5) gives the best results with alkali metal halides, but it can be used (with some reservations) with other uni-univalent electrolytes as well.

Having evaluated the heterogeneous component, we can now calculate an approximate value of the homogeneous component of the thermopotential.

Since the heterogeneous effect is the entropy of the electrode reaction, it also gives a measure of the heat of the electrode reaction when multiplied by the absolute temperature (local Peltier effect). Evidently, the magnitude and sign of the thermal effect must be determined by the difference between the entropy of the metal and the partial entropy of the metal ion.

6. ENTROPY OF TRANSFER IN THE SALT

As the diagram of the thermogalvanic cell (Fig. 1) shows, a potential gradient $\nabla\varphi_i$ arises in the electrolyte as a result of the presence of a temperature gradient. The work done by the passage of one Faraday of electricity through the electrolyte ($F \cdot \nabla\varphi$) appears in the form of heat absorbed or evolved by the electrolyte, depending on the direction of the current and on the sign of the potential gradient $\nabla\varphi_i$. This thermal effect, known as the heat of transfer, corresponds to the Thomson effect. The heat of transfer, divided by the temperature, defines a new parameter: the entropy of transfer in the salt, denoted by $\overset{*}{S}_i$. Naturally, for a given temperature gradient, the magnitude and sign of the potential gradient in the electrolyte ($\nabla\varphi_i$) must be a function of the nature of the fused electrolyte: for example, for a symmetrical electrolyte like KCl having a cation and an anion of comparable mobility the potential gradient will be small, and conversely for a unipolar cationic conductor like AgCl the potential gradient will be quite large. If the conductivity type in the fused electrolyte is a sensitive function of temperature, the potential gradient will also change with temperature.

Thus, the entropy of transfer in the electrolyte is a direct measure of the structural features of the fused salt. Since the entropy of transfer [see Eqns. (4) and (4')] is defined as a difference, its confidence limits are set by the uncertainty in the heterogeneous component of the thermopotential.

Physically, the entropy of transfer in the salt ($\overset{*}{S}_i$) is a manifestation of the migration of ions accompanying the passage of current through the electrolyte. If the heterogeneous component of the thermopotential is known with sufficient accuracy, the calculated entropy of transfer can be related to transport phenomena in the fused electrolyte (conductivity, self-diffusion, transport number), and can be treated as a structural characteristic determined by the nature of the chemical bond. The discontinuous change in transfer parameters which occurs at the melting point is reflected in a sharp change in the entropy of transfer.

The entropies of transfer of uni-univalent fused electrolytes are compared in Table 2. It can be seen that alkali metal chlorides have a small entropy of transfer: in other words, their thermopotential is determined mainly by the heterogeneous component, and only Joule heat is evolved by the passage of current through these electrolytes. For the most symmetrical of these electrolytes (KCl) the entropy of transfer is almost zero. In fused copper and silver halides the entropy of transfer is appreciable, not surprisingly since their structure is more complex than that of the alkali metal halides. In fused silver nitrate and silver sulphate the calculated $\overset{*}{S}_i$ values are +7.5 e.u. (at 550°K) and +7.7 e.u. (at 950°K) respectively, showing that the presence of a complex anion leads to anomalous $\overset{*}{S}_i$ values. This effect may be ascribed to a significant potential gradient in a direction opposite to that of the thermo-e.m.f. of the cell.

Table 2. Entropy of transfer in single fused salts.

Electrolyte	Temp., °K	Entropy of transfer, e.u.	Reference	Electrolyte	Temp., °K	Entropy of transfer, e.u.	Entropy of transfer, e.u.
LiCl	1100	—1.0	1	CuI	900	—6.0	6
NaCl	1300	—0.3	1	AgF	800	—3.5	5
KCl	1300	—0.2	1	AgCl	900	—3.4	8
RbCl	1000	—1.5	2	AgBr	900	—4.2	13
CsCl	950	—1.7	2	AgI	900	—5.4	6
CuCl	900	—3.5	4	$AgNO_3$	550	+7.5	14
CuBr	900	—5.1	6	Ag_2SO_4	930	+7.7	17

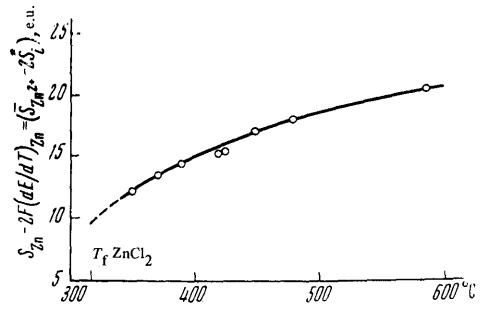


Figure 3. Variation of $(\bar{S}_{Zn^{2+}} - 2\overset{*}{S}_i)$ with temperature for the thermogalvanic cell $Zn_{T_2}|ZnCl_2|_{T_1}Zn$.

The entropy of transfer of bivalent metal salts may be discussed by considering a thermogalvanic cell with fused zinc chloride and liquid zinc electrodes. Inserting known values of S_{Zn} and $(dE/dT)_{Zn}$ into the thermopotential equation we can obtain the algebraic sum $(\bar{S}_{Zn^{2+}} - 2\overset{*}{S}_i)$: this quantity is found to increase by more than 11 e.u. over the temperature range between the melting point of $ZnCl_2$ and 600° (Fig. 3). The contribution of $\bar{S}_{Zn^{2+}}$ to this increase cannot be more than a few entropy units, since the entropy of zinc chloride increases by approximately 8.7 e.u. in this temperature range and the partial entropy of the zinc ions can only account for a fraction of this increase. It follows that the entropy of transfer in fused zinc chloride

is a fairly large quantity which decreases with temperature (in absolute value). Thus, the quantity $\overset{*}{S}_i$ may be added to the list of strongly temperature-dependent properties of fused $ZnCl_2$ (electrical conductivity, viscosity, self-diffusion[40,41]). The lack of constancy of $\overset{*}{S}_i$ is consistent with the polymeric network model of the structure of zinc chloride, which has been postulated[42] on the basis of Raman scattering studies.

At temperatures close to the melting point, the dissociation of zinc chloride with formation of simple ions is negligible, owing to polymerisation. Few current carriers are present, and fairly large potential gradients can develop. On raising the temperature the polymers are broken down and a simpler structure begins to appear, tending towards the structure of ionic melts (for which the entropy of transfer is small).

A more detailed analysis of the entropy of transfer is not justified as long as only tentative values of this parameter are available.

7. DEPENDENCE OF THE THERMOPOTENTIAL AND ITS COMPONENTS UPON THE STATE OF AGGREGATION OF THE ELECTRODES AND THE ELECTROLYTE

In the majority of thermogalvanic cells with a single fused salt (Table 1) the thermopotential has a negative sign and is almost independent of temperature. A barely significant change of thermopotential with temperature has been observed in sodium and potassium chloride[1], zinc and tin iodide[20], and lead bromide[3]. Measurements[18] on the cell $Zn_{liq.\,T_2}|ZnCl_{2melt}|_{T_1}Zn_{liq.}$, which were subsequently confirmed[20], indicate a more substantial and complicated temperature dependence of the thermopotential. Between 420 and 600° the thermopotential of fused zinc chloride changes sign (from positive to negative), showing a discontinuity at the melting point of zinc (Fig. 4).

Changes in thermopotential with temperature are due to structural changes in the fused electrolyte, and should therefore be observed in all electrolytes over a sufficiently wide range of temperature.

We shall discuss the discontinuous change in thermopotential accompanying a change in the state of aggregation of the electrodes for the particular case of the thermogalvanic cell consisting of fused zinc chloride with zinc electrodes. Applying Eqn. (4) to the cell

$$\underset{T_0}{W}\ \ldots\ W\,|\,\underset{T}{Zn}_{liq.(sol.)}\,|\,ZnCl_{2\,melt}\ \ldots\ |\,\underset{T+dT}{Zn}_{liq.}\,|\,W\ \ldots\ \underset{T_0}{W}$$

we can write

$$2F\left(\frac{dE}{dT}\right)_{Zn\,liq.} = -\Delta S + 2(\bar{\bar{S}}_e^{Zn\,liq.} - \bar{\bar{S}}_e^{W}) - 2\overset{*}{S}_e^{Zn\,liq.} + 2\overset{*}{S}_i$$

where $\Delta S = S_{Zn(liq.)} - \bar{S}_{Zn^{2+}} - 2\bar{S}_e^{Zn(liq.)}$, $(\bar{\bar{S}}_e^{Zn(liq.)} - \bar{\bar{S}}_e^{W})$ is the thermopotential of the Zn(liq.)/W couple, $\overset{*}{S}_e^{Zn(liq.)}$ is the entropy of transfer of electrons in liquid zinc, $\overset{*}{S}_i$ is the entropy of transfer in the salt.

After simplification we arrive at the expression

$$2F\left(\frac{dE}{dT}\right)_{Zn\,liq.} = S_{Zn\,liq.} - \bar{S}_{Zn^{2+}} - 2s_e^{W} + 2\overset{*}{S}_i$$

Similarly, for the cell with solid zinc, we can write

$$2F\left(\frac{dE}{dT}\right)_{Zn\,sol.} = S_{Zn\,sol.} - \bar{S}_{Zn^{2+}} - 2s_e^{W} + 2\overset{*}{S}_i$$

The difference between these equations is

$$2F\left[\left(\frac{dE}{dT}\right)_{Zn\,liq.} - \left(\frac{dE}{dT}\right)_{Zn\,sol.}\right] = S_{Zn\,liq.} - S_{Zn\,sol.} = \Delta S_{f(Zn)}$$

Thus, the difference in thermopotential between two cells measured close to and on either side of the melting point of zinc gives the entropy of melting of zinc.

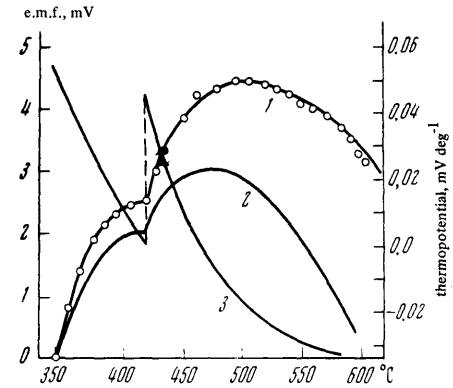


Figure 4. *1*) e.m.f. of the thermogalvanic cell $W|Zn_{T_2}|ZnCl_{2melt}|_{T_1}Zn|W$ against temperature of the "hot" electrode; *2*) ditto, for the thermogalvanic cell $Zn_{T_2}|ZnCl_{2melt}|_{T_1}Zn$; *3*) variation of thermopotential with temperature.

In our approximate, graphical determination, the jump in thermopotential at the melting point (see Fig. 4) is 0.05—0.052 mV deg^{-1}, giving an entropy of melting of 2.3—2.4 e.u. The tabulated value[43], obtained from calorimetric measurements of the heat of melting, is 2.48 e.u.

Table 3.

Electrolyte	T, °C	$F\left(\frac{dE}{dT}\right)_{Ag}$ e.u. crystal	$F\left(\frac{dE}{dT}\right)_{Ag}$ e.u. crystal	$\Delta F\left(\frac{dE}{dT}\right)_{Ag}$ e.u.	$(\bar{S}_{Ag^+})_{melt} - (\bar{S}_{Ag^+})_{cryst.}$ e.u.	$\overset{*}{S}_{i\,cryst.} - \overset{*}{S}_{i\,melt}$
AgCl	455	—14.10	—9.30	—4.8	(+2.2)	(—7.0)
AgI	558	—11.30	—11.30	0	(+1.35)	(—1.35)
$AgNO_3$	210	—5.45	—7.35	+1.9	(+2.86)	(—0.96)

Writing Eqn. (4) for the liquid and the solid electrolyte, and subtracting the two expressions, we obtain

$$F\cdot\left[\left(\frac{dE}{dT}\right)_M^{liq.} - \left(\frac{dE}{dT}\right)_M^{cryst.}\right] = (\overset{*}{S}_i^{liq.} - \overset{*}{S}_i^{cryst.}) - (\bar{S}_{M^+}^{liq.} - \bar{S}_{M^+}^{cryst.})$$

Evidently, since $\bar{S}_{M^+}^{liq.} > \bar{S}_{M^+}^{cryst.}$, the second term on the right-hand side is negative. In absolute value, $\overset{*}{S}_i^{cryst.} > \overset{*}{S}_i^{liq.}$, and therefore the first term is positive (since $\overset{*}{S}_i > 0$). The combined effect of these two terms may be a decrease or an increase in thermopotential at the transition from crystalline to fused electrolyte. As a special case, the

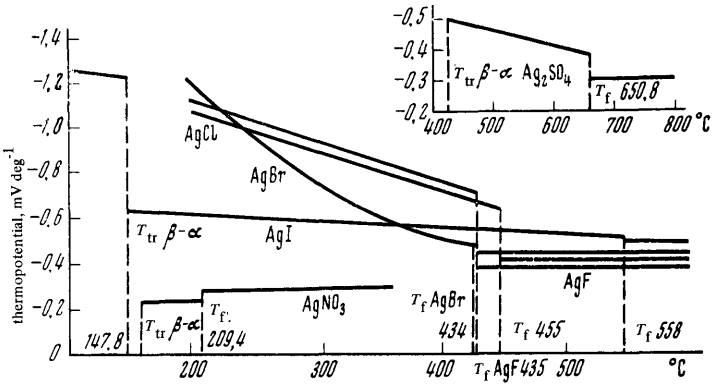


Figure 5. Temperature dependence of the thermopotential of the thermogalvanic cell $Ag_{T_2}|AgX|_{T_1}Ag$ (X = F, Cl, Br, I, NO_3, SO_4), from published data.

thermopotential may remain constant at the melting point of the electrolyte.

The measurements on thermogalvanic cells with AgCl, AgI, and $AgNO_3$ electrolytes, summarised in Table 3, provide examples of each type of thermopotential change at the melting point of the electrolyte.

Though the total thermo-effect can show different types of change at the melting point of the crystalline electrolyte, the entropy of transfer decreases in every case, because unipolar conduction (in the crystal) is replaced by mixed conduction (in the melt).

Fig. 5 shows thermopotential curves for cells with metallic (silver) electrodes and silver salt electrolytes over a wide temperature range. The curves have been compiled from published data.

New data on the entropy of transfer in solid and in fused salts are needed in order to provide more accurate values of ΔS_i^*, the change in entropy of transfer at the melting point, a very important parameter which reflects structural changes in the salt on melting. The first measurements of this type, reported by French workers[47], are consistent with a discontinuous change in the chemical bond of silver halides at the melting point.

8. APPLICATIONS OF THE THERMOPOTENTIAL

Leaving aside the possible application of thermogalvanic cells as converters of thermal into electrical energy, we can list some applications of thermo-e.m.f.'s in the study of the electrochemistry of fused salts.

Thermogalvanic corrosion. If the temperature of the surface of a reversible metal electrode is not uniform, a thermo-e.m.f. is developed between regions at different temperatures. Thermogalvanic corrosion is the result of current flow through this short-circuited thermogalvanic cell: the hotter regions are dissolved anodically, and metal is deposited on the cooler regions (usually in the form of dendrites). Thermogalvanic corrosion is often observed in practice.

Local Peltier effect. Electrolysis under isothermal conditions is accompanied by the absorption of heat in the regions where metal is dissolving anodically and heat evolution where metal is cathodically deposited. Hence, the passage of current through an isothermal electrode—fused electrolyte—electrode system converts it into a non-isothermal system: the temperature of the anode decreases, and that of the cathode increases with respect to the temperature in the bulk of the electrolyte. This phenomenon has been observed experimentally during the anodic dissolution and cathodic deposition of copper in a melt of cuprous chloride[46].

The sign and magnitude of the thermal effect accompanying, say, the anodic dissolution of a metal can be obtained from the measured thermopotential or calculated from the difference between the entropy of the metal and the partial ionic entropy of the same metal. Three cases are possible: the entropy of the metal and the partial entropy of the ion are approximately equal (resulting in a negligible thermal effect); the entropy of the metal is significantly smaller than the partial entropy of the ion (resulting in a large and positive thermal effect, i.e. heat absorption); the entropy of the metal is significantly larger than the partial entropy of the ion (resulting in a large and negative thermal effect, i.e. heat evolution). The thermal effect for cathodic reactions has the opposite sign.

Instances of all three cases are found in the calculations for systems with uni-univalent electrolytes summarised below.

$Cu_{sol.}|CuCl_{liq.}$ System

M.p. CuCl = 703°K; $S_{CuCl(liq.)}$ at 703°K is 36.9 e.u.[44]; S_{Cu} at 703°K is 13.2 e.u.[44]; $\bar{S}_{Cu^+}$ = 19.3 e.u.; ΔS = +6.1 e.u.; $T\Delta S$ = +4.3 kcal g-equiv^{-1}

$Ag_{sol.}|AgCl_{liq.}$ System

M.p. AgCl = 728°K; $S_{AgCl(liq.)}$ at 728°K is 39.8 e.u.[44]; S_{Ag} at 728°K is 15.8 e.u.[44]; $\bar{S}_{Ag^+}$ = 21.5 e.u.; ΔS = +5.7 e.u.; $T\Delta S$ = +4.15 kcal g-equiv^{-1}

$Li_{liq.}|LiCl_{liq.}$ System

M.p. LiCl = 880°K; $S_{LiCl(liq.)}$ at 880°K is 33.5 e.u.[44]; $S_{Li(liq.)}$ at 880°K is 15.7 e.u.[44]; $\bar{S}_{Li^+}$ = 14.3 e.u.; ΔS = −1.4 e.u.; $T\Delta S$ = −1.2 kcal g-equiv^{-1}

$Na_{liq.}|NaCl_{liq.}$ System

M.p. NaCl = 1073°K; $S_{NaCl(liq.)}$ at 1073°K is 40.8 e.u.[37]; S_{Na} at 1073°K is 23 e.u.[37]; $\bar{S}_{Na^+}$ = 19.8 e.u.; ΔS = −3.2 e.u.; $T\Delta S$ = −3.5 kcal g-equiv^{-1}

$K_{gas}|KCl_{liq.}$ System

M.p. KCl = 1043°K; b.p. K = 1030°K; $S_{KCl(liq.)}$ at 1045°K is 42.2 e.u.[37]; S_K at 1043°K is 44.87 e.u.[44]; $\bar{S}_{K^+}$ = 21.1 e.u.; ΔS = −23.77 e.u.; $T\Delta S$ = −24.8 kcal g-equiv^{-1}

$Rb_{gas}|RbCl_{liq.}$ System

M.p. RbCl = 995°K[45]; b.p. Rb = 952°K; $S_{RbCl(liq.)}$ at 995°K is 44.3 e.u.[45]; $S_{Rb(gas)}$ at 995°K is 48 e.u.[37,43,38]; $\bar{S}_{Rb^+}$ = 23.5 e.u.; ΔS = −24.5 e.u.; $T\Delta S$ = −24.4 kcal g-equiv^{-1}

$Cs_{liq.}|CsCl_{liq.}$ System

M.p. CsCl = 918°K; S_{CsCl} = 45 e.u.[45]; $S_{Cs(liq.)}$ at 918°K is 30.3 e.u.[37,43,38]; $\bar{S}_{Cs^+}$ at 918°K is 24 e.u.; ΔS = 5.9 e.u.; $T\Delta S$ = −5.4 kcal g-equiv^{-1}

It can be seen from these results that for solid metals the heat of anodic dissolution is appreciable, and its sign corresponds to absorption of heat; on the other hand, when the metal is in the vapour state its ionisation involves the evolution of a large amount of heat. When the state of aggregation of a metal electrode changes, a discontinuity occurs in the thermal effect. For liquid metals the thermal effect is small: this observation is consistent with the absence of chemical polarisation during the cathodic deposition of liquid metals. The small cathodic polarisation observed when solid metals are deposited is most probably a thermo-e.m.f. arising because of the difference in temperature between the polarised electrode and the reference electrode.

Electrocrystallisation of metals. The cathodic deposition of metals under non-isothermal conditions (i.e. in the presence of a temperature gradient) gives different types of deposit depending on the direction of the thermal field. In one direction, the operation of the short-circuited thermogalvanic cells assists the formation of a dendritic deposit, in the other direction it opposes dendrite formation. Of course, this effect is appreciable only when the thermopotential of the cell is fairly large.

Temperature coefficient of the electrode potential. The temperature coefficient of the e.m.f. of an isothermal chemical cell is the algebraic sum of the temperature coefficients of the two electrode potentials. Hence we can write

$$\Delta S = S_{MX} - S_M - \frac{1}{2}S_{X_2} = \left(\bar{S}_{X^-} - \frac{1}{2}S_{X_2}\right) - (\bar{S}_{M^+} - S_M)$$

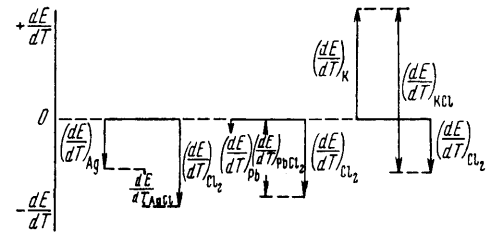


Figure 6. Temperature coefficient of the e.m.f. of a chemical cell as the algebraic sum of the temperature coefficients of the electrode potentials.

The terms in brackets (the heterogeneous components of the thermopotentials) are proportional to the temperature coefficients of the electrode potentials, which are added or subtracted (depending on their sign). Three possible cases are shown schematically in Fig. 6. For fused AgCl the temperature coefficient of the e.m.f. of the chemical cell $Ag|AgCl_{liq.}|Cl_2$ is equal to the difference between the temperature coefficients of the electrode potentials; for fused $PbCl_2$, $(dE/dT)_{PbCl_2}$ is equal to the temperature coefficient of the potential of the chlorine electrode; for fused KCl, $(dE/dT)_{KCl}$ is equal to the sum of the temperature coefficients of the electrode potentials.

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Further work on thermogalvanic cells with one-component electrolytes should be aimed at the following objectives. The experimental measurements should be extended to salts on which no data are yet available (in particular, bromides and iodides, and also fused oxides); there is also a need for a method of direct experimental measurement of the local Peltier effect (the heterogeneous component of the thermopotential), in order to obtain more precise data on partial ionic entropies and on the entropy of transfer in the salt (the homogeneous component of the thermopotential). Only then will it be possible to seek a quantitative relationship between the entropy of transfer and other kinetic parameters of the salt. The comparative studies of thermoelectric phenomena in crystals and in their melts should also continue, in order to throw new light on the nature of the melting process in crystalline salts.

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