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THERMODYNAMICS OF THERMOCELLS WITH FUSED OR SOLID ELECTROLYTES

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ABSTRACT

The thermodynamic principles related to thermocells are reviewed. The equation for the potential of a cell with a single component electrolyte, such as a fused or solid salt, is similar to that for a cell with aqueous solution electrolyte after the Soret equilibrium has been established. In particular the total "transported entropy" of the ionic species reacting at the electrodes may be obtained without any complication from transference numbers and values of this quantity are given for several cells.

The meaning and measurability of the partial molal entropies of single ions in electrolytes are considered. It is found that the transported entropy of metal ions in fused salts is approximately equal to estimated values of the partial molal entropies of these ions; hence the entropies of transfer are small. In solid electrolytes the entropies of transfer are sometimes large and are discussed in terms of the probable conductance mechanisms.

Through the years several thermocells with fused salt or solid salt electrolytes have been investigated.¹⁻⁵ Recent

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- (1) L. Poincaré, Ann. chim. phys., [6] 21, 289 (1890).
 - (2) H. Reinhold and A. Blachny, Z. Elektrochem., 39, 290 (1933);
H. Reinhold, Z. anorg. allgem. chem., 171, 181 (1928).
 - (3) H. Holtan, Thesis, Utrecht (1953); Tids. Kjemi Bergvesan Met., 12, 5 (1952).
 - (4) B. R. Sundheim and J. Rosenstreich, J. Phys. Chem., 63, 419 (1959)
 - (5) B. F. Markov, Doklady Akad. Nauk S.S.S.R., 108, 115 (1956).
-

work in other fields gives us now a clearer picture of the conduction mechanism in the solid electrolytes as well as additional data for the liquids. Also some of the previous discussions of these thermocells are confused unnecessarily by apparent uncertainties in transference number. Hence it seems worthwhile to look again at the information on these systems.

Thermodynamic Relationships.- The thermodynamics of a thermocell was derived by Eastman⁶ and in greater detail by

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- (6) E. D. Eastman, J. Am. Chem. Soc., 50, 292 (1928).
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Wagner⁷. We shall follow the definitions and terminology of

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- (7) C. Wagner, Ann. Physik., 3, 629 (1929); 6, 370 (1930).
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Agar and Breck⁵ and confine our attention to cells with pure

(8) J. N. Agar and W. G. Breck, Trans. Faraday Soc., 53, 167 (1957).

metal electrodes and simple MX_v electrolytes where X is a halogen or nitrate. The EMF of the cell E is defined as the electrical potential of a wire attached to the hot electrode less the potential of a similar wire attached to the cold electrode. The electrical work for v equivalents of electricity is determined by the entropy absorbed from the heat reservoir surrounding the hot electrode when this positive electricity passes through the cell from the cold to the hot electrode. This entropy is equal to the sum of the entropy absorbed in the electrode reaction, in this case $\underline{S}_M - \bar{\underline{S}}_M^{+v} - v\bar{\underline{S}}_{e-(M)}$ and the entropy transported away from the hot electrode region, in this case $-\underline{S}_M^{*+v} - v\underline{S}_{e-(M)}^*$. Here $\underline{S}_M$ is the molal entropy of the metal, $\bar{\underline{S}}_M^{+v}$ and $\underline{S}_M^{*+v}$ are the partial molal entropy and the entropy of transfer, respectively, of the M^{+v} ion, and $\bar{\underline{S}}_{e-(M)}$ and $\underline{S}_{e-(M)}^*$ are the corresponding properties of the electron in the metal M. These terms may be combined to yield

$$v F \frac{dE}{dT} = \underline{S}_M - \bar{\underline{S}}_M^{+v} - v\bar{\underline{S}}_{e-(M)} \quad (1)$$

where $\bar{\underline{S}}_M^{+v}$, the total "transported entropy" of the ion M^{+v} , is the sum of the partial molal entropy of the ion and the entropy of transfer. The quantity $\bar{\underline{S}}_{e-(M)}$ is, similarly, the "transported entropy" of electrons in the metal M.

It is desirable to note at this point the relationship to aqueous solution thermocells. After the Soret equilibrium is established, equation (1) is applicable to the corresponding aqueous solution cell, but at uniform electrolyte concentration in each half cell the expression contains the additional term $t_-(S_M^{*+v} + vS_X^{*-})$ where t_- is the transference number of the negative ion. In the aqueous solution the sum of the two ionic entropies of transfer is the quantity which governs the Soret equilibrium. However, in a pure salt the transfer of both ions equally in the same direction is just the gross linear movement of the salt which has no net entropy of transfer. Hence the sum $(S_M^{*+v} + vS_X^{*-})$ is zero and it is apparent that the transference number drops out of the equation for the pure salt cell. Indeed a transference number in a single component fused salt can only be defined in an arbitrary manner. While the transference measurements for solid electrolytes by Tubandt⁹ yield information of interest for

(9) C. Tubandt, Handbuch Exp.-Physik XII, 1, 394 ff., Leipzig (1932).

interpretation of the conduction mechanism, there is no need to introduce a transference number in the thermodynamic equation for a pure salt either solid or liquid.

In equation (1) the first quantity on the right is just the molal entropy of the metal which is available from heat

capacity data and the third law.¹⁰ Recently Tempkin and Khoroshin¹¹

(10) D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Solvents", American Chemical Society, Washington, D. C., 1956.

(11) M. I. Tempkin and A. V. Khoroshin, Zhur. Fiz. Khim., 26, 500 (1952).

have given values for $\bar{S}_e^-$ in several metals; these values are zero within the uncertainty of presently available thermocell data. Thus equation (1) yields $\bar{S}_M^{+v}$ from experimental thermocell potentials. Several values obtainable from the literature for fused salts are listed in Table I and similar values for solid electrolytes are given in Table II.

Absolute Ionic Entropies in Fused Salts.- While it is not yet experimentally feasible to measure directly the partial molal entropies of individual ions, a rather convincing theoretical calculation seems possible in favorable cases. Consider first a fused salt wherein the positive and negative ions are identical in every respect except for the sign of the net electrical charge on each. In this case clearly the symmetry of the situation allows one to divide the measured molal entropy equally between the positive and negative ions.

Next let us consider the effects of various differences between the ions. The mass effect on the translational entropy is well known and gives a difference $(3/2) R \ln (\underline{M}_2/\underline{M}_1)$ between the entropies of species of molecular weights $\underline{M}_2$ and $\underline{M}_1$.

TABLE I

THERMOCELLS WITH FUSED SALT ELECTROLYTES

Electrolyte	Ref.	T, °K	S_M	$-vF \frac{dE}{dT}$	$\bar{S}_M^{v+}$	$\bar{S}_M^{v+}$	S_M^{*v+}
$AgNO_3$	3,4	500	13.37	7.6	21.0	19	2
$AgCl$	2,3,5	800	16.43	9.3	26	22	4
$AgBr$	2,5	750	16.00	11.	27	22	5
AgI	2,5	850	16.84	10.	27	24	3
$ZnCl_2$	1	~ 600	14.41	-6	8	14	-6
$SnCl_2$	1	~ 600	20.59	+1	22	16	+6

TABLE II
THERMOCELLS² WITH SOLID SALT ELECTROLYTES

Electrolyte	T, °K	S_M	$-vF \frac{dE}{dT}$	$\bar{S}_M^{v+}$
AgCl	400	11.98	32	44
	500	13.37	27.6	41.0
	600	14.55	23.1	37.6
	700	15.55	16.2	31.8
AgBr	400	11.98	34	46
	500	13.37	25.8	39.2
	600	14.55	18.2	32.8
AgI (II)	400	11.98	28.6	40.6
AgI (I)	500	13.37	12.9	26.3
	600	14.55	12.9	27.4
CuCl	400	9.70	23	33.
	500	11.07	21.5	32.6
	600	12.22	19.8	32.0
CuBr	400	9.70	36	46.
	500	11.07	29.5	40.6
	600	12.22	22.8	35.0

TABLE II (cont.)

Electrolyte	T, °K	S_M	$-vF \frac{dE}{dT}$	$\bar{S}_M^{v+}$
CuI (III)	400	9.70	23	33.
	500	11.07	21.5	32.6
	600	12.22	19.8	32.0
CuI (I)	750	13.66	8	22.
PbCl ₂	500	18.87	27	48.
PbBr ₂	500	18.87	21	40.
PbI ₂	550	19.55	-18	2.
	650	21.65	-9.2	12.5

Moderate differences in the short range forces which determine ion size should have no effect since ions of the same sign will seldom contact one another. Consequently the entropy of the metal ion in a simple binary salt is given by the expression

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

Wagner⁷ estimated the entropy of the ion to be just one half that of the salt which is our result except for the omission of the mass correction term.

The entropies of free rotation and of vibration of polyatomic ions are readily calculated by standard methods and can be subtracted from the total entropy before apportionment of the translation entropy. In actual cases, however, the rotation will usually be somewhat restricted. If a reasonable estimate can be made of the potential barrier restricting the rotation, then the net internal entropy can also be estimated.

If one type of ion is very much larger than the other, then there will be direct short range repulsive contacts of the large ions. This effect is well known in ionic crystals such as LiI where the anion-anion contacts primarily determine the size of the unit cell. In such cases one expects the freedom of translational motion of the large ions to be less than that of the small ions. It is difficult to calculate

the magnitude of this difference but it seems unlikely to exceed a few cal/degree mole except in most extreme cases.

If we apply these methods to AgNO_3 at 500°K and assume a 4.5 cal/deg mole reduction in rotational entropy of NO_3^- from restriction of rotation, the net internal entropy of NO_3^- is 19.7 cal/deg mole. The heat capacity of silver nitrate has been measured and the data as summarized by Kelley¹²

(12) K. K. Kelley, U. S. Bureau of Mines Bulletins 477 and 584, U. S. Government Printing Office, Washington, D. C., 1950 and 1960.

yield the entropy value 54.04 cal/deg mole at 500°K . With the mass correction of equation (2) one then finds

$$\bar{S}_{\text{Ag}^+} = 19.0 \text{ cal/deg mole in fused } \text{AgNO}_3 \text{ at } 500^\circ\text{K}.$$

The calculation of the partial molal entropy of silver ion in the fused halides follows the same principles but is simplified by the absence of internal entropy for the anions. The results, based upon Kelley's tables, are given in Table I. No correction has been made for anion-anion repulsions in these values; such effects would further restrict anion motion and reduce the anion entropy. Consequently, the cation entropies would be increased by this effect which may or may not be significantly large.

Entropies of Transfer in Fused Salts. - The last column in Table I gives the values of the entropy of transfer which

follow from the experimental data and our calculation of the absolute ion entropies. In a simple MX salt in the liquid state all of the ions are presumably free to migrate without large activation energy. Nothing in the nature of the fused salt seems to indicate any other source of significant heat of transfer. Consequently, we expect the heat and entropy of transfer to be small for the various silver salts. The values of $\underline{S}^*$ in Table I are indeed small and may be further reduced by a modest correction to $\underline{S}$ for anion-anion repulsion effects.

Ionic Entropies in Solid Electrolytes.- In accordance with the usual definition the partial molal entropy of an ion in a solid electrolyte is the increase in the total entropy of the solid upon addition of extra ions divided by the molal amount of ions added. Space charge effects will actually limit additions to very small amounts in the case of ions. If the lattice of the solid electrolyte were perfect, this process of addition would be difficult to interpret, but actual crystals at finite temperatures contain significant numbers of defects such as vacancies. The actual addition process is readily interpreted in terms of these defects. For example in the silver halides the defects are predominantly vacancies in the positive ion lattice and interstitial positive ions. Suppose there are $\underline{N}_1$ vacancies and correspondingly $\underline{N}_1$ interstitials per mole of silver halide. The addition of $\underline{N}_2$ excess silver ions, where $\underline{N}_2 \ll \underline{N}_1$, will yield a final state in which there are $\underline{N}_2$ more interstitials than vacancies. One can

easily show that the equilibrium state after the addition will have approximately $(N_1 + 1/2 N_2)$ interstitial atoms and $(N_1 - 1/2 N_2)$ vacancies.

While it is possible to define equilibrium entropies of interstitial ions, vacancies, etc., and to express the partial molal entropy of ions in the solid in these terms, there are no experimental values now available for comparison. However, this discussion indicates the mechanisms by which extra ions may be accommodated in crystals containing defects.

Transported Entropy of Ions in Solids.- We now turn to the discussion of the experimentally measured total transported entropy of the positive ion. The actual conduction mechanism must be considered. Mott and Gurney,¹³ Wagner¹⁴ and Hauffe¹⁵

(13) N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals", Oxford University Press, 1948.

(14) C. Wagner, J. Electrochem. Soc., 99, 346C (1952).

(15) K. Hauffe, "Reaktionen in und an Festen Stoffen", Springer-Verlag, Berlin-Göttingen-Heidelberg, 1955.

have reviewed work which indicates for the systems of Table II conductance by three types of carriers: (a) interstitial cations, (b) cation vacancies, (c) anion vacancies. In the case of conduction by interstitial cations the transported entropy is just the sum of the partial molal entropy of the interstitial ion and its entropy of transfer. In the other cases the cation

produced at the electrode either fills a cation vacancy in case (b) or extends the lattice and creates v anion vacancies in case (c); also there are the entropies of transfer of the respective vacancies. These results are summarized by the equations

$$(a) \quad \bar{S}_{M^{+v}} = \bar{S}_{M,O} + S_{M,O}^* \quad (3a)$$

$$(b) \quad \bar{S}_{M^{+v}} = (\bar{S}_M^1 - \bar{S}_{M,\square}) - S_{M,\square}^* \quad (3b)$$

$$(c) \quad \bar{S}_{M^{+v}} = (\bar{S}_M^1 + v\bar{S}_{X,\square}) + vS_{X,\square}^* \quad (3c)$$

where M,O indicates an interstitial cation, $M,\square$ or $X,\square$, cation or anion vacancies, respectively, and $\bar{S}_M^1$ is the entropy of a cation in an ideal lattice site.

While it is not feasible to calculate these various entropy quantities accurately, certain properties may be defined which make estimates possible. The partial molal entropies of defects all contain terms for the entropy of distribution over the possible sites which have the form $-R \ln x_1$ where x_1 is the ratio of defects to sites. In many cases $x_1 \approx 10^{-4}$ which yields an entropy term of ~ 18 cal/deg mole which is a positive contribution in cases (a) and (c) but negative in (b). The entropy of thermal vibration of the cation also enters either in $\bar{S}_{M,O}$ or $\bar{S}_M^1$ (but not for vacancies), and its magnitude may be estimated to be approximately the same as the entropy of the metal $\underline{S}_M$. The entropies of transfer may be expected to be positive and of the order of the energy of activation for ion migration divided by the temperature.

In the case of AgBr, Teltow¹⁶ gives energies of activation of

(16) J. Teltow, Ann. Physik., [6] 5, 63, 71 (1949); Z. physik. Chem., 195, 197, 213 (1950).

approximately 2.5 kcal/mole for interstitial cations and 5.5 kcal/mole cation vacancies. Combination of these values for AgBr in the 400-600°K range yields the estimates for $\bar{S}_M + v$ of 35 to 45 cal/deg mole for case (a) and -5 to -15 cal/deg mole for case (b).

In the best studied case of AgBr Teltow's results¹⁶ indicate that at 400°K the conductance is almost entirely by interstitial ions, case (a), and the value of $\bar{S}$ in Table II is reasonable on this basis. At 500 and 600°K, respectively, the vacancy conduction is reported to constitute approximately 10% and 30% of the total, and this shift of part of the current to mechanism (b) is rather more than sufficient to explain the reduction of $\bar{S}$ with increase in temperature. The properties of the other silver and cuprous halides^{13,14} are sufficiently similar to AgBr to indicate a parallel explanation, but the available data are much less detailed.

Tubandt⁹ reports 100% anion transference for PbCl₂ and PbBr₂ but about 50% for PbI₂ at the temperature of interest. Since vacancy mechanisms are presumably involved, we may assume mechanism (c) for the chloride and bromide and half (b) - half (c) for the iodide. However, Mott and Gurney¹³ show that many of the data indicate conductance on the surfaces

rather than through the lattice. Hence it seems best to merely note qualitative agreement between the large values of $\bar{S}$ found for PbCl_2 and PbBr_2 with the expectation for mechanism (c) and the lower value for PbI_2 with the expectation for the mixture of mechanisms (b) and (c).

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