Experimental and Theoretical Study of the "Intrinsic Contribution" to the Heat of Transport *, **

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The thermotransport of divalent Sr, Cd and Mn ions in silver chloride and bromide has been investigated experimentally. A model for the intrinsic contribution to the heat of transport is proposed. This model is used to interpret our experiments, together with other experiments reported in the literature, namely the thermoelectric power of pure silver chloride and bromide, and the thermotransport of antimony in silver and copper metals.

I. Introduction

Numerous studies of thermomigration have been performed in recent years, but at the present time they show a great deal of disagreement, both in the theoretical understanding and in the experimental work. Theories are multiple, and frequently they are compared with too few experimental data or with data which are imprecise. Hence comparisons of theories with experiments are not too significant. Therefore we thought it was necessary to attempt first to get a consistent set of precise experimental results, and secondly to study the different available theories.

Our experiments of thermotransport of divalent cations in silver chloride and bromide are first reported. Then follows a critical discussion of previous theories, which will be used later to interpret these experiments. Finally, an interpretation is also given for other experiments reported in the literature, namely, the thermoelectric power of these pure halides and the thermotransport of antimony in silver and copper metals.

II. Thermotransport of Divalent Radioactive Cations in Silver Chloride and Bromide

In these halides, the very high diffusion coefficients render the standard method of the steady state quite feasible. The experimental procedure has been described in detail elsewhere [1]. The samples are Harshaw crystals whose purity is around 10 ppm. The sample is spring loaded between two graphite blocks, one of them being cooled (Fig. 1). The whole is placed in a furnace. After the anneal, the sample is studied by a standard method: microtoming, weighing of the cuttings and γ counting. The experimental concentration of tracer is plotted versus the reciprocal of the temperature in a semi-log plot (Figs. 2 and 3). For cadmium, especially in the bromide, the scatter is due to counting difficulties, but for strontium and manganese, the curves are always very well behaved. The slopes of these

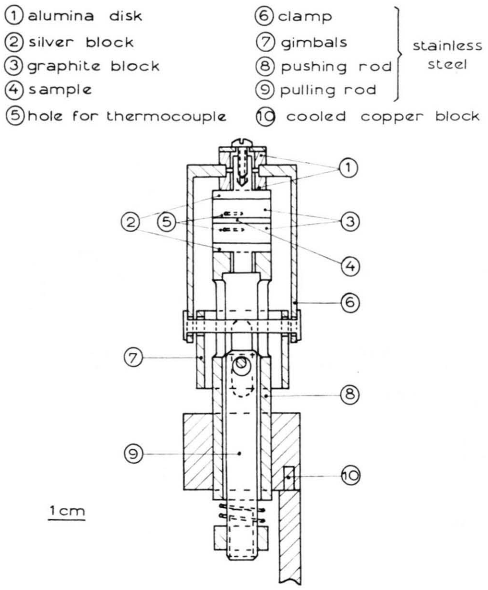

Fig. 1. Experimental apparatus.

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** This paper is based on a thesis which will be submitted in 1971 in partial fulfillment of the requirements for the degree of Docteur es Sciences Physiques at the Faculté des Sciences d'Orsay (France).

[1] J. L. CROLET, Rapport DEM/SRMP-1780, 1970.

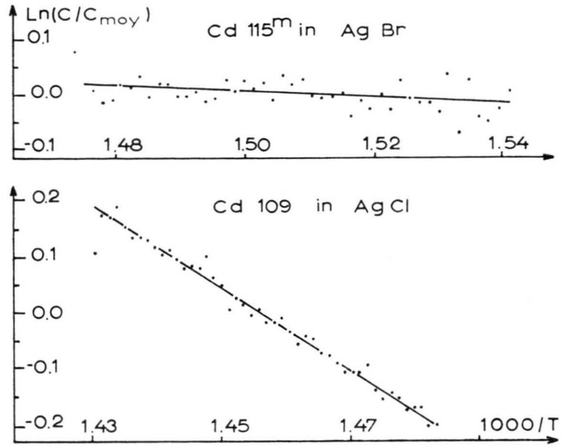

Fig. 2. Experimental curves. a) Run B 7: Cd 115^m in AgBr; b) Run C 10: Cd 109 in AgCl.

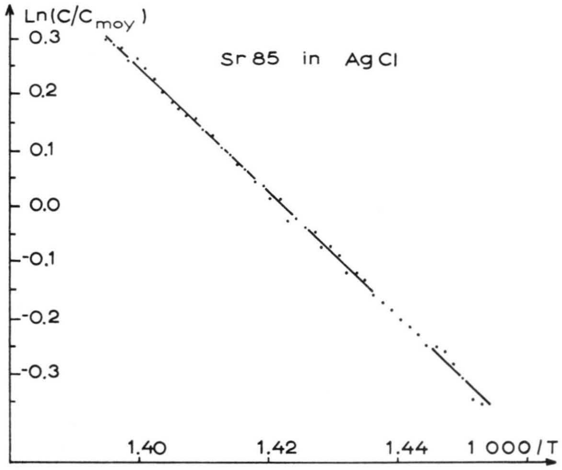

Fig. 3. Experimental curve for Run C 8: Sr 85 in AgCl.

straight lines define the effective heats of transport. They are given in Table 1. The reproducibility of the measurements has been checked [1] and the scatter never exceeds the indicated errors.

Table 1.

Matrix	Ion	$\overline{Q}$ in eV	Temperature range
AgCl	Sr^{++}	-1.0 ± 0.1	$335 < t < 445$ °C
	Cd^{++}	-0.62 ± 0.06	$390 < t < 440$ °C
	Mn^{++}	-0.56 ± 0.05	$400 < t < 435$ °C
AgBr	Cd^{++}	0.0 ± 0.1	$370 < t < 415$ °C
	Mn^{++}	0.0 ± 0.1	$360 < t < 415$ °C
		-0.25 ± 0.15	$320 < t < 360$ °C

III. Critical Study of Existing Theories

1. The thermodynamics of irreversible processes

The basic approach to the thermotransport is the thermodynamics of irreversible processes (TIP). It relates the fluxes of heat and diffusing species to generalized forces. The heat of transport of a species is defined as the heat flux associated with the unit flux of that component in isothermal conditions. The reduced heat of transport is defined as the remainder of the associated flux after removing the heat flux corresponding to the purely geometrical displacement of the diffusing particle. The reduced heat of transport equals the heat of transport minus the partial enthalpy of the diffusing entity. This enthalpy is the reversible part of the heat of transport and represents the reversible transport of energy induced by a virtual, infinitely slow translation of the particle. The reduced heat of transport is the irreversible part of the heat of transport and arises because the microscopic transport of heat is not infinitely slow in an actual jump of the particle. Conversely, in a thermogradient, the sense of the thermotransport corresponds to an associated heat flux flowing from the hot to the cold side. The role of the TIP is to relate these two conjugate effects, namely thermotransport and heat flow induced by isothermal diffusion. Consequently, when only one of these effects is considered, the interest of the TIP is decreasing. Anyway, atomistic theories are needed to calculate the heats of transport. Such theories may be subdivided into 2 general types: the Wirtz-Brinkman-Le Claire theory and the heat carrier scattering.

2. The Wirtz-Brinkman-Le Claire Theory [2]

In this theory, the temperature is assumed to be defined at any position in the crystal. Then, the jump frequencies are assumed to be proportional to Boltzmann's exponentials corresponding to the local temperature at the initial position of the jumping ion. From these assumptions, it can be shown that in the case of self diffusion by a vacancy or an interstitial mechanism, the reduced heat of transport equals the migration enthalpy h_m. These two assumptions have to be discussed. From the thermodynamical view point, the local temperature does

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[2] K. Wirtz, Z. Phys. **44**, 221 [1943]. — J. A. Brinkman, Phys. Rev. **93**, 345 [1954]. — A. D. Le Claire, Phys. Rev. **93**, 344 [1954].

not exist. Even though it may be defined by continuous interpolation between macroscopically defined temperatures, it cannot be used in Boltzmann's exponentials because it is not consistent with the temperature definition in these statistics. It can be introduced only in continuous functions of temperature, defined themselves by interpolation. Thus, the Wirtz theory becomes questionable.

3. The Heat Carrier Scattering Theory

To explain the asymmetry of the jump frequencies in a thermogradient, and by analogy with electrotransport, some authors have used the concept of a driving force, acting on the ions during their jumps. In most cases, this driving force is thought to be due to the scattering of the heat carriers, electrons and phonons, by the diffusing species. The driving force is thus an electromechanical force. HUNTINGTON[3] however, proposed to separate the heat of transport into additive terms including the effects of the heat carriers scattering and the so called intrinsic contribution of the Wirtz theory.

4. General Kinetic Theory

An original treatment of the thermotransport has been developed by MANNING[4] in his book. He studies the correlated walk of ions in a thermogradient. Thus, the knowledge of the frequencies of all possible jumps is needed.

Let us consider two lattice sites at the abscissae 0 and d. As far as only first order effects are taken into account, the average value Γ_{m} of the jump frequencies of the ion, $\Gamma_{0\mathrm{d}}$ and $\Gamma_{\mathrm{d}0}$, is identical with the average of the 2 isothermal frequencies Γ_0 and Γ_{d} corresponding to the local temperatures at sites 0 and d.

$$\Gamma_{0\mathrm{d}}+\Gamma_{\mathrm{d}0}=2\,\Gamma_{\mathrm{m}}=\Gamma_0+\Gamma_{\mathrm{d}}\,,$$
$$\Gamma_{0\mathrm{d}}-\Gamma_{\mathrm{d}0}=\Gamma_{\mathrm{m}}(d/k\,T)\,F_{\mathrm{eff}}\,. \tag{1}$$

The difference between these 2 inverse jump frequencies may be expressed in terms of an effective driving force F_{eff}, proportional to grad T/T.

$$F_{\mathrm{eff}}=-\tilde{q}\,\mathrm{grad}\,T/T=-(q^*-h_{\mathrm{f}})\,\mathrm{grad}\,T/T. \tag{2}$$

The effect of the actual vacancy concentration gradient is explicitly taken in account by defining

$$h_{\mathrm{f}}=\frac{k\,T^2}{\mathrm{grad}\,T}\,\frac{\mathrm{grad}\,x}{x} \tag{3}$$

where x is the actual vacancy concentration at the site occupied by the vacancy before the jump. In Eq. (2), the coefficient q^* expresses a first order effect and thus, can be separated into additive terms. It is not a heat of transport, although it plays an analogous role. Once given the q^*'s of all couples of inverse jumps, Manning's calculation leads to a general expression of the fluxes of the diffusing species and allows the different effective heats of transport to be calculated.

It is thus a very attractive tool, because it keeps the q^*'s as unknown quantities and does not use hypotheses on the effect of the thermogradient. Both kinds of thermotransport theories can be introduced in order to define the q^*'s. Thus the actual driving force due to the scattering of the heat carriers leads to a contribution q^*_{scatt}. We will see later that sums such as $h_{\mathrm{m}}+q^*_{\mathrm{scatt}}$ lead to a fairly good agreement between the experimental and calculated effective heats of transport, but first, let us present an alternative derivation and try to generalise the concept of intrinsic contribution h_{m} to q^*.

5. The Intrinsic Contribution to the Heat of Transport

Instead of the two inverse jumps 0, d and d, 0, let us consider the two opposite jumps 0, ± d. The probability that a vancancy exists at sites ± d is the molar concentration of vacancies $x_{\pm\mathrm{d}}$ at these sites. The jump frequencies of an ion into this adjacent vacancy is from (1), (2), and (3)

$$\frac{\Gamma_{0,\,\pm\mathrm{d}}}{x_{\pm\mathrm{d}}}=\left(\frac{\Gamma_0}{x_{\mathrm{d}}}\right)_{\mathrm{grad}\,T=0}\left(1\pm q'^*\,\frac{d}{2\,k\,T}\,\frac{\mathrm{grad}\,T}{T}\right), \tag{4}$$
$$q'^*=h_{\mathrm{m}}-q^*\,. \tag{5}$$

Comparison between Eqs. (1) and (4) points out the formal kinetic character of this effective driving force, whose definition corresponds either to q^* or to q'^* according to whether inverse or opposite jumps are considered. On the other hand, from Eqs. (4) and (5) follows that, if q^* equals h_{m}, an ion at the local temperature T, jumps into an adjacent vacancy with the same frequency as in an isothermal crystal at this temperature T, on whichever side, hot or cold, the vacancy may be located. This is another formulation of Wirtz's idea but this form may be established more easily by considering the har-

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[3] H. B. HUNTINGTON, J. Phys. Chem. Sol. **29**, 1641 [1968].

[4] J. R. MANNING, Diffusion Kinetics for Atoms in crystals.

monic vibrations of the crystal. FLYNN[5] has shown that the atomic jumps could be thought reasonably to be induced by random interference of these vibrations. Since in a thermogradient, only the amplitudes of the waves are changed, the elongations remain symmetrical and do not favour any particular jump direction. The complete calculation is reported in Ref. [1]. This derivation is very general and applies to self and heterodiffusion by a vacancy or interstitial mechanism. The intrinsic contribution h_m to q^* comes from the total lack ($q'^* = 0$) of any directional effect due to the harmonic terms of the vibrations. Paradoxically, h_m is much larger than the contribution due to phonon scattering, that is to the anharmonic terms. In the following, it is shown that good agreement with the present experiments can be obtained by assuming $q^* = h_m$ if allowance is made for vacancy supersaturations. We return now to the experimental results.

IV. Interpretation of the Experiments

In the present case, the anionic sublattice may be considered as perfect and fixed. The cationic one is also fixed in the absence of electrical current. The effective heat of transport is thus the heat Q^{**} calculated by Manning under the assumption of tightly bound vacancy impurity complexes.

$$\overline{Q} = Q^{**} = h_{m2} - 2\, h_{m1} + h/2 - h_a\,. \qquad (6)$$

Here, it is assumed that $q_j^* = h_{mj}^*$. Also h_{m2} and h_{m1} are the migration enthalpies of the exchange and non dissociative jumps of the vacancy, h_a is the association enthalpy of the complex and h defines the actual vacancy concentration gradient. In the case of local equilibrium of defects, h is the formation enthalpy of a Frenkel pair.

In the domain involved, that is in the intrinsic domain, h and the vacancy supersaturation are given by a self diffusion study. From the condition of zero electric current, it follows that the silver interstitial and vacancy fluxes are equal and have the following form

$$J = R\left[(Q_i^* - Q_s^*)\, \frac{\operatorname{grad} T}{T} + k\,T\, \frac{\operatorname{grad}(x_i\, x_v)}{x_i\, x_v} \right]$$
$$R = \frac{L_{ii}\, L_{ss} - L^2_{is}}{L_{ii} + L_{ss} + 2\, L_{is}}\,. \qquad (7)$$

[The derivation of Eq. (7) [1] follows the now classical analysis of ALLNATT and CHADWICK[6].] R is related to the Onsager's coefficients L and is some average of the vacancy and interstitial mobilities. The Q^*'s and the x's are the heat of transport and the molar fraction of defects. These fluxes are not necessarily zero or even constant. Thus, they have to be created or absorbed at the sample extremities by superficial sources and sinks of defects. Likewise, internal sources and sinks must provide their divergence. Thus, the following equations are to be solved.

$$J = F_{\text{surf}}\,, \qquad \operatorname{div} J = F_{\text{int}} \qquad (8)$$

where F is the flow of the sources and sinks. In the case of the steady state, F can be shown to be [1]:

$$F = K\,(x_i\, x_v - x_F^2)\,; \qquad (9)$$

x_F is the equilibrium concentration of Frenkel pairs.

K measures the efficiency of a given kind of source and sink. It is also shown [1] that the electroneutrality remains valid to the first order. Finally, still to the first order, for very high K, the solution of Eqs. (8) requires the bracket of (9) to have a zero value. Conversely, for very low K, the solution is J or $\operatorname{div} J = 0$. There are thus four limiting possibilities according to the infinite or zero efficiency of the internal or superficial sources and sinks. As soon as a kind of source is efficient, there is local equilibrium. However, the variations of the fluxes through the sample are different and depend on which kind of source and sink is efficient (Fig. 4).

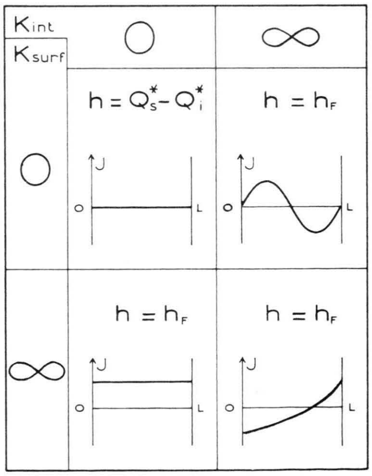

Fig. 4. Schematic diagram of the four possible types of defect behaviour.

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[5] C. P. FLYNN, Phys. Rev. **171**, 682 [1968].

[6] A. R. ALLNATT and A. V. CHADWICK, Trans. Faraday Soc. **62**, 1726 [1966].

Conversely, when none of the sources and sinks is efficient, there is a very large supersaturation of defects, corresponding to an apparent enthalpy of formation $h_0 = Q_s^* - Q_i^*$ in Eq. (6). The effective heats of transport of the divalent cations have been calculated in both cases, where there is a supersaturation ($\overline{Q}_0$) or where there is local equilibrium ($\overline{Q}_F$). The results are gathered in Table 2.

Table 2.

System		h_{m2}	h_{m1}	h_a	$\overline{Q}_F$	$\overline{Q}_0$	$\overline{Q}$
AgBr	Cd	0.55 [a]	0.30 [i]	0.21 [a]	0.27	−0.16	0.0 ±0.1
				0.16 [e]	0.32	−0.11	
	Mn	0.74 [b]	0.34 [i′]	0.22 [b]	0.37	−0.06	0.0 ±0.1
AgCl	Cd	0.61 [c]	0.38 [i]	0.37 [c]	0.15	−0.42	−0.62 ± 0.06
				0.27 [e]	0.20	−0.33	
				0.47 [f]	0.10	−0.52	
			0.29 [g]	0.37 [c]	0.33	−0.24	
				0.27 [e]	0.38	−0.15	
				0.47 [f]	0.28	−0.34	
	Mn	0.56 [b]	0.31 [g]	0.28 [b]	0.33	−0.24	−0.56 ± 0.05
	Sr	[d]	0.4 [i″]	[d]	0.2	−0.4	−1.0 ±0.1
			0.6 [i″]		−0.2	−0.8	

[a] J. E. Hanlon [7]
[b] P. Süptitz, R. Weidman [8]
[c] B. G. Lure, A. N. Murin, I. V. Murin [9]
[d] A. L. Laskar, A. P. Batra, L. Slifkin [10]
$h_{m2} + h_F/2 - h_a = 0.98$
} diffusion

[e] P. Müller [11]
[f] H. C. Abbink, D. S. Martin [12]
} electrical conductivity

[g] I. Kunze, P. Müller [13] ionic thermocurrent
[i] H. Böttger [14] dielectric loss
[i′] estimated from values for Cr^{++} and Fe^{++}
[i″] estimated (orders of magnitude)

Values of h_F and h_0 used in calculating values of $\overline{Q}_F$ and $\overline{Q}_0$ are taken from references [e] and [f], as indicated below:

Matrix	h_F	h_0	Reference
AgCl	1.44	0.20	f
	1.25	0.20	e
AgBr	1.06	0.20	e

For Mn^{++} in the bromide, the value h_{m1} is interpolated between those of ions Cr^{++} and Fe^{++}. For strontium, there are no measurements either and the indicated values are only orders of magnitude. Altogether, the experimental $\overline{Q}$ and the calculated $\overline{Q}_0$ agree fairly well.

Thus, the interpretation of the heats of transport needs 3 steps: Manning's calculation, the model for the intrinsic contribution to the q*'s, finally the hypothesis that the internal and superficial sources and sinks of defects are inefficient. These 3 steps, and especially the last one, are corroborated by the interpretation of thermopower measurements in these pure halides.

V. Thermoelectric Power of Pure Silver Halides

1. *Theory*

The thermoelectric power S is the sum of 2 effects:

- the homogeneous thermopower S_{hom}, corresponding to the thermoelectric field $S_{\text{hom}} \operatorname{grad} T$ in the bulk of specimens;
- the heterogeneous thermopower S_{het}, corresponding to the difference $S_{\text{het}} \operatorname{grad} T$ between the surface potentials at the hot and cold extremities of specimens

$$S = S_{\text{hom}} + S_{\text{het}}. \tag{10}$$

a) Homogeneous Thermopower

The internal thermoelectric field can be calculated together with Eq. (7). Its values are the following:

– local equilibrium ($h = h_F$):

$$S_{\text{hom}} = [t_i(Q_i^* + h_F/2) + t_s(Q_s^* - h_F/2)]/e\,T \tag{11 a}$$

– supersaturation ($h = h_0$):

$$S_{\text{hom}} = (Q_i^* + Q_s^*)/2\,e\,T. \tag{11 b}$$

The t's are the transport numbers of the interstitial and substitutional silver ions.

b) Heterogeneous Thermopower

At high temperature, the space charge region is a very thin layer close to the surface. In this region,

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[7] J. E. Hanlon, J. Chem. Phys. **32**, 1492 [1960].

[8] P. Süptitz and R. Weidmann, Phys. Stat. Sol. **27**, 631 [1968].

[9] B. G. Lure, A. N. Murin, and I. V. Murin, Soviet Phys. Solid State **9**, 1337 [1967].

[10] A. L. Laskar, A. P. Batra, and L. Slifkin, J. Phys. Chem. Sol. **30**, 2061 [1969].

[11] P. Muller, Phys. Stat. Sol. **21**, 693 [1967].

[12] H. C. Abbink and D. S. Martin, J. Phys. Chem. Sol. **27**, 205 [1966].

[13] I. Kunze and P. Müller, Phys. Stat. Sol. **33**, 91 [1969].

[14] H. Böttger, Phys. Stat. Sol. **4**, 669 [1964].

the main source of point defects is the surface and not the dislocations. To the first order, the fluxes of defects are conservative between the bulk and the space charge region and so are the generalized forces acting on a given kind of defect. Assuming that the thermal forces are equal in both regions leads to the equation:

$$\left(-k\,T\,\frac{\operatorname{grad} x}{x}\pm e\operatorname{grad} V\right)_{\text{bulk}} = \left(-k\,T\,\frac{\operatorname{grad} x}{x}\pm e\operatorname{grad} V\right)_{\text{space charge}} \qquad (12)$$

where V is the electrical potential and x the molar fraction of defects. The signs + or − hold respectively for vacancy and interstitial. Since in the space charge region, the operator gradient separates into a direct dependence versus the abscissa y and an indirect one through the temperature gradient, let us write V and x in the form (Fig. 5)

$$V = V_1(y) + V_2(T)\,,\quad x = x_1(y)\;x_2(T)\,. \qquad (13)$$

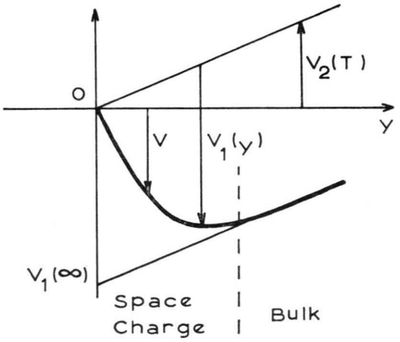

Fig. 5. Sketch of the electric potential V near an interface in a thermogradient.

A solution of Eq. (12) is obtained by taking the same functions of the temperature in the bulk and in the space charge region. The functions of the abscissa become the solutions of the system:

$$k\,T\,\frac{\mathrm{d}\,\operatorname{Log} x_1}{\mathrm{d}y}\pm e\,\frac{\mathrm{d}V_1}{\mathrm{d}y}=0\,, \qquad (14)$$
$$x_1(\infty)=1\,,\qquad V_1(0)=0\,.$$

In the case of local equilibrium, this system is identical to the one used to determine the equilibrium distribution of defects near an isothermal interface[15]. Thus, the heterogeneous thermopower is the temperature derivative of the surface potential

$$S_{\text{het}}=\frac{\mathrm{d}}{\mathrm{d}T}\,V_1(\infty)\,. \qquad (15)$$

In other cases but the local equilibrium, the actual value of S_{het} remains unknown.

2. Comparison with Experiments

Figure 6 shows the experimental curves of CHRISTY[16], and of PATRICK and LAWSON[17], obtained with silver electrodes. The dashed lines represent the calculated homogeneous thermopower in the case of local equilibrium. The letters A and M refer to ABBINK et al.[12] and MULLER's[11] migration enthalpies used for the Q^*'s in Eq. (11 a). The corresponding values calculated under the assumption of supersaturation are quite different from both view points of the magnitude and the temperature dependence. For the heterogeneous thermopower, unfortunately, the surface potential determinations do not allow it to be calculated, even in the case of local equilibrium. REINHOLD and BLACHNY's estimations[18] are quite rough and have no quantitative

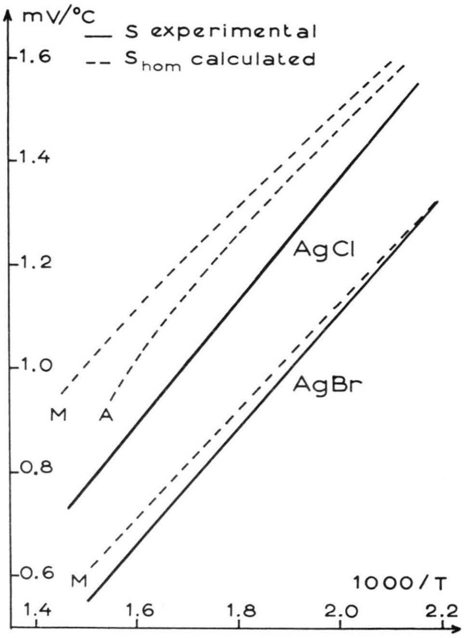

Fig. 6. Temperature dependence of the experimental thermopower and of the calculated homogeneous thermopower.

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[15] J. L. CROLET, Rapport CEA R-3972, 1970.

[16] R. W. CHRISTY, J. Chem. Phys. **34**, 1148 [1961].

[17] L. PATRICK and A. W. LAWSON, J. Chem. Phys. **22**, 1492 [1954].

meaning. Qualitatively however, they do not predict any large temperature dependence. Likewise Kliewer's determination of surface potential of silver chloride in vacuum[19], leads to a constant value $-0.23\ \mathrm{mV}/^\circ\mathrm{C}$ which agrees fairly well with thermopower measurements with silver electrodes. Nonetheless, in Fig. 6, the agreement is more significant for the slopes than for the magnitudes.

Once more, the interpretation of the experiments involves an assumption about the efficiencies of the sources and sinks of defects. From the preceding section, the internal sources and sinks must be inefficient. On the other hand, the superficial ones are efficient in presence of silver, but inefficient in presence of graphite. This is consistent with the model of source and sink which we used to derive the expression (9) of their flow. In this model, the sources are thought to be double jogs, one in the cationic sublattice and the other one in the anionic sublattice. Since we asumed that the anions do not move, the cationic jog is compelled to vibrate between the two positions surrounding the anionic jog. During these oscillations, a silver ion is absorbed or emitted and the jog may act as vacancy or interstitial source or sink. But in any case, it cannot act twice in the same way. For example, after absorbing an interstitial, it must absorb a vacancy (or create a new interstitial) before it can absorb another interstitial. Therefore, these sources and sinks are easily saturable and are inefficient in most cases. On the other hand, exchange of silver ions between a silver electrode and the surface of the halide, can prevent the sources and sinks from saturating and thus enhances their efficiency.

Since the method used to predict the intrinsic contribution to the heats of transport, seems to be successful in the case of insulators where this contribution is by far the most important one, we will look now at metals.

VI. Thermotransport in Metals

To avoid experimental and theoretical uncertainties, the discussion will be restricted to the thermotransport of antimony in silver and copper, measured respectively by **Biermann** et al.[20] and **Hehenkamp**[21] using the steady state method. In gold, unfortunately, the published experiments involve the thin layer method which does not allow the exact meaning of the measured values to be determined[22]. The effective heat of transport of antimony is $\overline{Q}$:

$$\overline{Q} = Q_{\mathrm{Sb}}^{**} - (D_{\mathrm{s}}/D_{\mathrm{Sb}})\, Q_{\mathrm{s}}^{**} \tag{16}$$

where D_{s} and $Q_{\mathrm{s}}{}^{**}$ are the self diffusion coefficient and the heat of transport of the solvent. [The subscript s in (16) and (17) refers to solvent atoms in general. For tracer atoms of the solvent, the diffusivity and the heat of transport are respectively $f\, D_{\mathrm{s}}$ and $Q_{\mathrm{s}}{}^{**}/f$, where f is the correlation factor for self-diffusion.] The defect supersaturation has been shown by **Gerl**[23] to be negligible. Thus the actual vacancy concentration gradient is related to the formation enthalpy h of the vacancy and the Q^{**} becomes

$$Q_{\mathrm{s}}^{**} = h_{\mathrm{m}0} - h\,. \tag{17}$$

The heat of transport of antimony (Q_{Sb}^{**}) separates into q_{e}^{*}, the electronic contribution, calculated by **Gerl**, and q_{int}^{*}, which is deduced from Manning's calculation and from the model for the intrinsic contribution to the q^{*}'s with the assumption that $q_{\mathrm{j}}{}^{*} = h_{\mathrm{mj}}$.

$$Q_{\mathrm{Sb}}^{**} = q_{\mathrm{e}}^{*} + q_{\mathrm{int}}^{*}\,, \tag{18}$$

$$\begin{aligned} q_{\mathrm{int}}^{*} &= h_{\mathrm{m}2} + 2\langle N_{\mathrm{p}}\rangle\, h_{\mathrm{m}0} + h_{\mathrm{a}} - h(1 + 2\langle N_{\mathrm{p}}\rangle) \\ &\quad + \frac{2}{2\,\omega_1 + 7\,F\,\omega_3}\Big[2\,\omega_1 (h_{\mathrm{m}0} - h_{\mathrm{m}1} - h_{\mathrm{a}}) \\ &\quad - 3\,\omega_3 \left(h_{\mathrm{m}0} - \frac{h_{\mathrm{m}3} + h_{\mathrm{m}4}}{2}\right)\Big]\,. \end{aligned} \tag{19}$$

$\langle N_{\mathrm{p}}\rangle$ and F are calculated by Manning. The effect of the thermoelectric field is very low and is not stated. The h_{m}'s are no longer measurable. On the other hand, they can be calculated by the Lazarus-Le Claire theory. The steps of this calculation are presented in Table 3.

Two interaction potentials have been used: Hartree and Thomas-Fermi. When one keeps in mind the approximations of the Lazarus-Le Claire theory, the agreement is fairly good, especially for the Thomas-Fermi potential. It is worth noting that this potential already gave very good predictions of the ΔQ's.

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[20] W. Biermann, D. Heitkamp, and T. S. Lundy, Acta Met. **13**, 71 [1965].

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[23] M. Gerl, Thesis, 91 Orsay (France) 1968.

VII. Conclusion

Three very different kinds of experiments in a thermogradient have been interpreted quite satisfactorily. We believe that this agreement is not fortuitous but is probably linked to a physical reality, which we should summarize as follows: the effect of a temperature gradient may be separated into the effect of the heat flux, through the scattering of the heat carriers by the diffusing species and into the effect of the position dependence of temperature. If one considers the jumps of an ion from a given site, the first effect does favour one particular jump direction, while the latter one does not but just makes the jump frequency depend on that lattice site. Both effects originate thermomigration. The first effect leads essentially to the now classical electronic contribution to the heat of transport of impurities in metals, while the second effect provides the intrinsic contribution and is quite general. As in the Wirtz theory, this intrinsic contribution is related to migration enthalpies. However, this relation now is much more complicated, involving several migration enthalpies, weighted by correlation parameters [†].

Table 3.

Solvent	Silver		Copper	
Temperature	870 °C		950 °C	
h	1.1		1.17	
h_{m0}	0.83		0.87	
q_e^*	−0.50		−0.12	
Q_s^{**}	−0.27		−0.30	
D_s/D_{Sb}	0.19		0.09	
Potential	Th.-Fermi	Hartree	Th.-Fermi	Hartree
h_a	0.076	0.229	0.122	0.300
$h_{m1}-h_{m0}$	0.035	0.116	0.054	0.145
$h_{m2}-h_{m0}$	−0.438	−0.423	−0.629	−0.709
$h_{m3}-h_{m0}$	0.010	0.069	0.017	0.079
ω_1/ω_3	0.78	0.62	0.70	0.54
ω_4/ω_0	1.95	5.07	2.69	8.02
$7F$	4.37	3.33	3.99	2.95
N_p	0.028	−0.260	−0.056	−0.404
q_{int}^*	−0.70	−0.42	−0.84	−0.59
Q_{Sb}^{**}	−1.20	−0.92	−0.96	−0.71
$\bar{Q}_{calc.}$	−1.15	−0.87	−0.93	−0.68
$\bar{Q}_{exp.}$	-1.26 ± 0.13		-1.22 ± 0.17	

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[†] *Note added:* In gold, a re-analysis of earlier data [22] shows the heats of transport of Sb impurity and solvent ions to be respectively:

$$Q_{Sb}^{**} = -3.5 \text{ eV}, \quad Q_s^{**} = 0.4 \text{ eV}.$$

Eqs. (18) and (17) lead to calculated values of Q_{Sb}^{**} and Q_s^{**} respectively −0.9 and −0.16 eV. It seems likely that these discrepancies may be attributed to a positive additional contribution to q_0^*.