INTERNATIONAL CENTRE FOR
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ELECTRON LOCALIZATION
AND THE NONMETAL–METAL TRANSITION
IN ALKALI–ALKALI HALIDE SOLUTIONS

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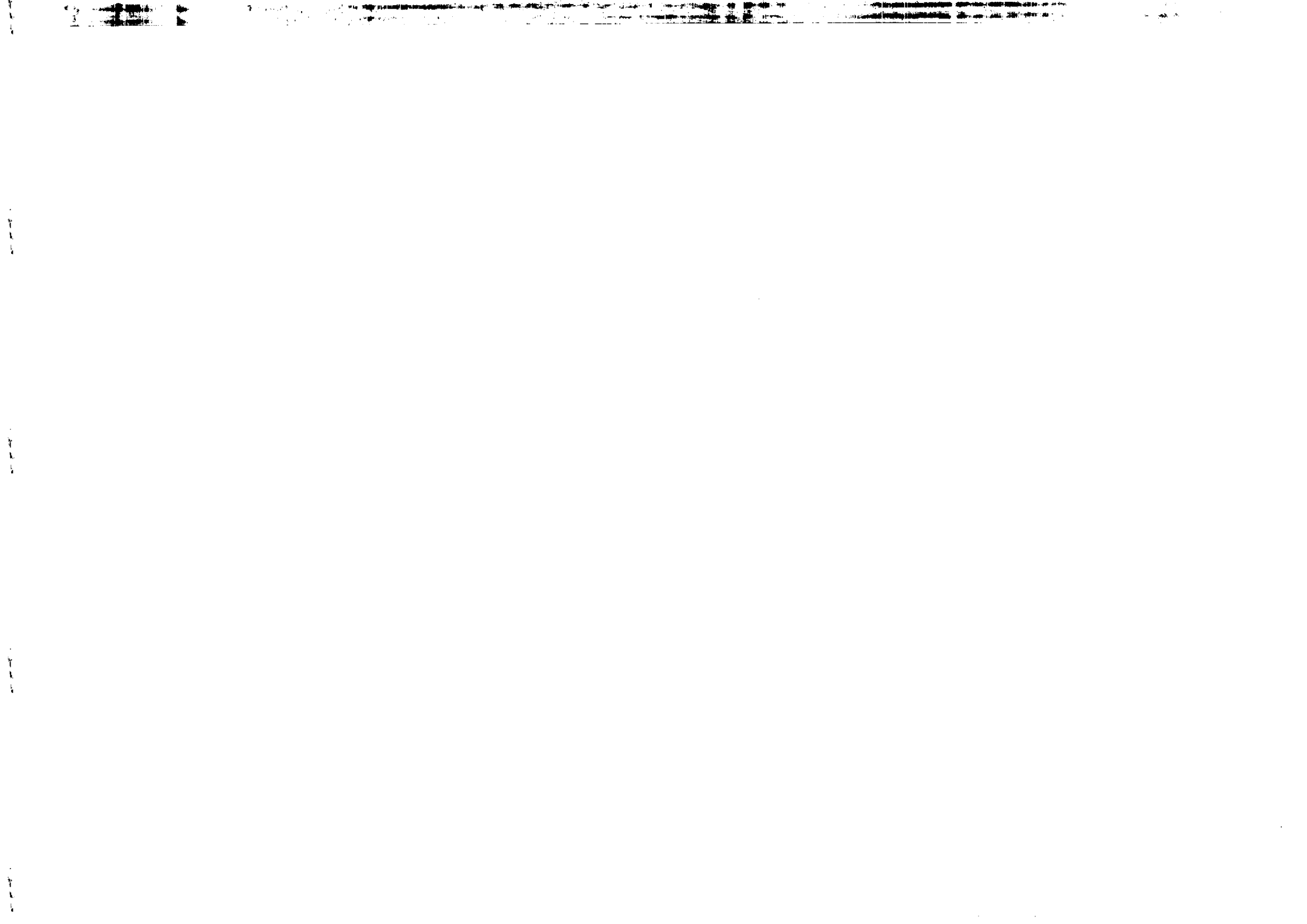**INTERNATIONAL
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ABSTRACT

We evaluate and extend an earlier proposal for a microscopic theory of the nonmetal-to-metal (NM-M) transition which occurs on dissolving an alkali metal in its molten halide. The transition is viewed as involving a balance between the free energy gain from the binding of valence electrons into localization centres and the excess free energy of the ionic assembly screened by the electrons. Using parameters estimated for solutions of potassium in potassium chloride and assuming that the elementary process of electronic trapping is the formation of F–centre like clusters, Thomas–Fermi screening by metallic electrons is shown to lead to a very sharp NM-M transition at a concentration in the range of 25-30% added metal. Thermally activated hopping of the localized electrons and the evolution of the localization centres with composition are next crudely taken into account by allowing for an additional contribution to the inverse screening length, which is estimated from the electronic localization length. This is shown to lead to a progressive break–up of the localization clusters, accelerating into a NM–M transition in the same concentration range. This simplified theoretical scenario is consistent with the available experimental evidence.

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1. Introduction

Solutions of metals in their molten halide salts and their nonmetal-to-metal (NM-M) transitions have attracted considerable attention for a number of years (for recent reviews see [1-4]). The mechanisms of localization of valence electrons in the salt-rich region of the phase diagram and their evolution with increasing concentration c of added metal towards the NM-M transition have been the object of especially intense and careful studies in the case of solutions of alkali metals in molten alkali halides. It is well established that in these systems at very high dilution trapping of single electrons occurs at favourable structural fluctuations with the help of a cooperative rearrangement of the ions. From simulation results on K-KCl [5, 6] the very old F-centre model for the localization site in this concentration regime has received substantiation and a microscopic description as consisting of an electron with a first-neighbour shell of about four K^+ ions on average, the electronic residence time being of the order of a few picoseconds. With increasing concentration of metal a reduction of unpaired spin densities [7] and the emergence of a new optical absorption band [8] have been observed, which indicate progressive formation of spin-paired states and small metallic clusters. The absorption associated with F-centre electrons is still present, however. The NM-M transition in K-KCl at $T \approx 800°C$ occurs at a concentration $c \approx 0.24$ [3], well below that of the critical point for demixing at $c = 0.39$. There is as yet no strong evidence that may allow one to attribute a specific (Anderson, Mott-Hubbard or percolation) type to the transition [9].

It has recently been proposed by Yurdabak, Akdeniz and Tosi [10] (hereafter to be referred to as I) that a microscopic theory of the NM-M transition in these systems would involve balancing the free energy gain from binding of valence electrons in localized states associated with ionic clusters and the free energy change from dissolving the components of such clusters into an ionic assembly screened by metallic electrons. The crucial consideration is that, as electrons are released into conduction states because of natural limitations on the available localization sites (e.g. the number of K^+ ions needed to form F-centre-like clusters), the onset of metallic screening would rapidly lead to a dissolution of the bound states and to a collective transition of the valence electron assembly to a metallic state. This argument, combined with the available simulation data [5], immediately suggests that the NM-M transition in K-KCl should be found at $c = 0.25$, in agreement with experiment. It was also shown in I that, by using at the simplest level of theoretical description a model of charged hard spheres for the ions and Thomas-Fermi screening for the metallic electrons, such a theory is amenable to an analytic solution within the mean spherical approximation (MSA).

In the present work we first evaluate the model proposed in I in its original form, using parameters appropriate to K-KCl at 800°C. The NM-M transition is indeed found to occur at $c = 0.25 - 0.30$ and to be extremely sharp. We then proceed to elaborate on the model by including some allowance for the finite lifetime of the localization clusters, due to thermally activated electron hopping, and for their evolution with composition. We show that this leads to a smooth, progressive dissolution of the localization centres and hence to a smooth transition to a metallic state, with an insignificant shift in its location.

2. The model and its parameters

Following I, we view a K-KCl mixture at chemical composition c of added metal as composed of $(K_4)^{3+}$ clusters in molar fraction cx, free K^+ ions in molar fraction $(1 - 4cx)$ and free Cl^- in molar fraction $(1 - c)$, with a residue of unbound "metallic" electrons in molar fraction $c(1 - x)$. The equilibrium value of x is to be determined by minimization of the Helmholtz free energy F at constant composition c, temperature T and molar volume v.

The free energy is written as

(1) $F = xcf_b + c(1 - x)E_g + F_t - TS_m + F_{ex}$

where f_b is the free energy of binding of a cluster relative to its constituents in vacuo, E_g is the ground state energy of unbound electrons, F_t is the ideal translational free energy, S_m is the ideal entropy of mixing and F_{ex} is the excess free energy arising from the interactions between the components of the melt. As shown in I, minimization of the free energy in eqn (1) with respect to x yields a law of mass action for the equilibrium concentration x_{eq} of bound clusters with an activation free energy which depends self-consistently on x_{eq}.

The excess free energy F_{ex} in eqn (1) can be estimated in analytic form by resorting to a model of charged hard spheres exponentially screened by the electrons with an electronic inverse screening length λ, the solution of such a model having been given in the MSA by Blum et al. [11, 12]. That is, the condition

(2) $c_{ij}(r) = -\dfrac{z_i z_j}{k_B T\, r}\, \exp(-\lambda r)$

is imposed on the Ornstein-Zernike direct correlation functions $c_{ij}(r)$ for $r > \frac{1}{2}(\sigma_i + \sigma_j)$, z_i being the ionic charges and σ_i the ionic diameters for the various components of the melt. Using also earlier results of Ginoza [13, 14] it was shown in I that this yields

(3) $F_{ex} = U_{ex} + k_B T \dfrac{\Gamma^2}{3\pi}(\Gamma + \frac{3}{2}\lambda)$.

where Γ is an ionic inverse screening length to be determined by solving self-consistently the equation

(4) $\Gamma^2 + \lambda\Gamma - (\pi/k_BT)\,D(\Gamma,\lambda) = 0$

and U_{ex} is the excess internal energy of the melt, which is given by

(5) $U_{ex} = -\Gamma \sum_i \dfrac{\rho_i\, z_i^2 \exp(-\lambda\sigma_i)}{1 + \sigma_i\Gamma\Phi_0(\lambda\sigma_i)} - \dfrac{\pi P_1^2}{2\Omega\Delta} - \Delta_N\left[P_1(\Gamma + \tfrac{1}{2}\lambda - \dfrac{\pi T_1}{2\Omega\Delta}) + P_0\right]$.

In these equations ρ_i are the partial ionic densities, $1 - \Delta = \tfrac{\pi}{6}\sum_i \rho_i\sigma_i^3$ is the packing fraction and
$\Phi_0(y) = [1 - \exp(-y)]/y$. Expressions for the quantities $D(\Gamma,\lambda)$, P_n, Ω, T_1 and Δ_N can be found
in the work of Ginoza [13, 14].

All the calculations that we report in the following will refer to the temperature $T = 800°C$
and make use of the data of Garbade and Freyland [15] for the molar volume v as a function of
composition. In the rest of this section we turn to assess the various parameters of the model.

Let us consider first the pure components at the two extreme values of the concentration
range. For pure molten KCl at 800°C we adopt the values $\sigma_K = 2.79$ Å and $\sigma_{Cl} = 3.05$ Å for the
ionic diameters, from the work of Senatore et al. [16]. Using these values in eqns (3)-(5) we get
$F = -823$ kJ/mol and $U_{ex} = -694$ kJ/mol. The latter value is in acceptable agreement with the
value $U_{ex} = -650.5$ kJ/mol from experiment at 760°C [2], since in a charged-hard-sphere model
no account is taken of the overlap repulsive energy between the ions. Most pleasingly the same
value for the ionic diameter of K$^+$, combined with the Thomas-Fermi expression for the inverse
screening length and with the value of E_g obtained by Vosko et al. [17] from a fit to quantal
Monte Carlo data, leads with eqns (3)-(5) to a very reasonable value for the free energy of pure
molten potassium at 800°C. This is $F = -262$ kJ/mol, which is to be compared with the
measured value $F = -265$ kJ/mol for liquid potassium at 63.5°C [18].

The evaluation of the free energy of the solution at any intermediate concentration
involves two further model parameters, i.e. the binding free energy f_b and the effective diameter
σ_c of a bound $(K_4)^{3+}$ cluster. We recall some relevant results from earlier calculations. Senatore
et al. [16] have estimated that the electron in an F-centre state is bound by 2-2.5 eV in a potential
well having an effective radius of roughly 3 Å. The quantal simulation results of Parrinello and
Rahman [5] for the electron - K$^+$ pair distribution function in an F-centre state show that the peak
of the distribution lies at a radius of about 2 Å and that four K$^+$ ions are contained within a radius
of about 4 Å. One should also bear in mind deviations from spherical shape of a $(K_4)^{3+}$ cluster
and the possibility of penetration by neighbouring halogens. In fact, an upper bound on the value
of σ_c is set by the requirement that the packing fraction of the solution should not appreciably
exceed that of pure molten KCl, i.e. $1 - \Delta \leq 0.6$. From the above we have been led to adopt $f_b = -170$ kJ/mol and $\sigma_c = 5$ Å as preferred values for illustrative purposes. This choice of σ_c is
compatible with an ionic packing fraction of about 0.6 over the whole nonmetallic range of the

solution. Neither the precise value of f_b nor that of σ_c (provided it is not larger than about 5 Å)
are critical for the results to be presented in the following sections.

3. Nonmetal-to-metal transition with pure Thomas-Fermi screening

Within Thomas-Fermi theory the metallic electrons, in molar fraction $c(1 - x)$ determine
the value of the inverse screening length λ as

(6) $\lambda_{TF} = \lambda_o\,[c(1 - x)v_K/v]^{1/6}$,

λ_o being the inverse Thomas-Fermi screening length in pure molten potassium and v_K the partial
molar volume of the metal in the solution. We adopt this expression for λ in this section, thus
omitting any account of screening of the ionic interactions from thermally activated hopping of
the localized electrons.

Minimization of the free energy yields in this case, with the choice of parameters
presented in section 2, that the localized states on clusters are completely stable over the range of
concentration $0 \leq c \leq \tfrac{1}{4}$. Namely, $x_{eq} = 1$ and $\lambda = 0$ over this range, a finite value of λ being
unfavoured by the loss of Coulomb excess energy that it entails (cf. the first term on the right-
hand side of eqn (5)). This result is stable against changes of f_b and σ_c within reasonable ranges,
as well as against changes in eqn (6) that would allow for the exclusion of metallic electrons
from the cores of halogen ions. The latter effect can be crudely taken into account by replacing
the total molar volume v in the denominator of eqn (6) by the partial molar volume v_K.

Once c exceeds the value $\tfrac{1}{4}$, however, the assumption made on the nature of the
localization sites as involving four potassium ions immediately forces a value for x_{eq} below unity
and hence a finite value for the inverse screening length. The result is a sharp increase of the
value of the free energy at equilibrium, leading to a sharp NM-M transition within a very narrow
range of concentration below $c = 0.3$. These behaviours are illustrated in Figure 1 for the
equilibrium number of bound electrons and in Figure 2 for the inverse screening length as
functions of composition. These figures also show that very little changes are found when the
value of the effective diameter σ_c is lowered from 5 Å to 4 Å.

Across the transition the calculated free energy of the solution shows an equally sharp
increase from the typical molten salt value $F = -760$ kJ/mol to the typical alkali metal value
$F = -290$ kJ/mol. Only slow changes of the free energy with concentration are found in the
nonmetallic region and in the metallic region of the solution.

4. Inclusion of screening by hopping electrons

As already briefly recalled in section 1, localization of electrons in salt-rich solutions of alkali metals in alkali halides is not due to the presence of static trapping centres, but involves a cooperative rearrangement of the ions around a favourable structural fluctuation. In turn, a localized electron is not permanently bound to its localization site, but hops out of it after an average residence time of the order of a few picoseconds. Evidently, this thermally activated hop involves dissolution of the localization centre.

The crucial concept which allows one to take some account for this type of cooperative electronic and ionic dynamics in the problem at hand is, we believe, that of the localization length for an electron in a state of hopping motion. Bearing in mind the above characteristics of the trapping and hopping processes, on the long time scale involved in thermodynamic properties the localization length should diverge in the high dilution limit $c \rightarrow 0$. It will, of course, also diverge at the NM-M transition. On the other hand, in the intermediate composition range between high dilution and the NM-M transition a finite localization length can result from the electron-electron interactions leading to spin-paired states and higher aggregates, as again briefly recalled in section 1.

In view of the foregoing we propose that the electronic localization length L should be of the same order as the mean distance between occupied localization centres, i. e. of order

(7) $L \approx (6v/\pi cx)^{1/3}$.

We also suggest that the hopping electrons can effect screening of the ionic interactions over lengths of the same order of magnitude.

Specifically, in the calculations that we report in this section we have adopted the following recipe for the inverse screening length λ to be used in eqns (3)-(5):

(8) $\lambda = [x\lambda_h^2 + (1 - x)\lambda_{TF}^2]^{1/2}$

with λ_{TF} given by eqn (6) and λ_h given by

(9) $\lambda_h = \alpha (\pi cx/6v)^{1/3}$.

The quantity α in eqn (9) is a numerical factor of order unity, which can be chosen so as to control the sharpness of the calculated NM-M transition.

Figures 3, 4 and 5 show the results that we have obtained with the choice $\alpha = 4$. It is seen from Figure 3 that the equilibrium number of $(K_4)^{3+}$ localization clusters decreases continuously across the salt-rich range of concentration, accelerating towards its vanishing point at $c \equiv 0.29$. Figure 4 shows the corresponding behaviours that we find for the two partial inverse screening lengths as well as for the total inverse screening length. At relatively high dilution minimization of the free energy is achieved by having $\lambda_{TF} \approx \lambda_h$, which implies that a finite

fraction of the electrons are available to effect metallic screening. These start to dominate the screening at $c \approx 0.15$, above which the pure Thomas-Fermi limit of the metallic state is rapidly approached while the localization length approaches its divergence at the NM-M transition.

Finally, Figure 5 reports the behaviour of the free energy as a function of concentration in the solution at equilibrium. There is quite a rapid, though continuous rise of F from the molten salt regime to the liquid metal regime across the NM-M transition region.

5. Summary and concluding remarks

As already remarked in 1, the pure Thomas-Fermi screening model that we have evaluated in section 3 would probably be more appropriate to describe a situation where the localized electronic state is strongly bound and its nature is little sensitive to variations of composition on the approach to the NM-M transition. Such a situation appears to be realized in solutions of some polyvalent metals in their molten halides.

For alkali - alkali halide solutions, on the other hand, thermally activated hopping of localized electrons and evolution of the localization centres with composition have clearly been established experimentally. We have been able to crudely account for them by assuming in section 4 that the localization length of hopping electrons plays a role in the problem as a measure of the distance over which these electrons can screen the ionic interactions in the melt, in parallel with Thomas-Fermi screening by electrons in free-conduction states. We have there displayed a smooth, progressive dissolution of the localization clusters and a smooth transition to a metallic state, still occurring in the model at $c \approx 25$-30 %. Such a theoretical scenario appears to be more in tune with that obtained from experiment on the evolution of the electronic assembly in alkali - alkali halide solutions towards the NM-M transition, as it was summarily recalled in section 1.

*   *   *

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Figure captions

Figure 1. - Equilibrium value x_{eq} of the fraction of bound electrons *versus* composition c in K-KCl at 800°C with pure Thomas-Fermi screening, for two choices of the diameter σ_c of the localization centres (full curve, $\sigma_c = 5$ Å; dashed, $\sigma_c = 4$ Å).

Figure 2. - Inverse Thomas-Fermi screening length λ_{TF} corresponding to the cases shown in figure 1.

Figure 3. - Equilibrium value x_{eq} of the fraction of bound electrons *versus* composition c in K-KCl at 800°C, with inclusion of screening by hopping electrons (full curve) and with pure Thomas-Fermi screening (dashed). The parameters used in the calculation are $\sigma_c = 5$ Å and $\alpha = 4$.

Figure 4. - Inverse screening length λ corresponding to the results shown in figure 3 (full curve) and its components λ_h (dashed) and λ_{TF} (dot-dashed).

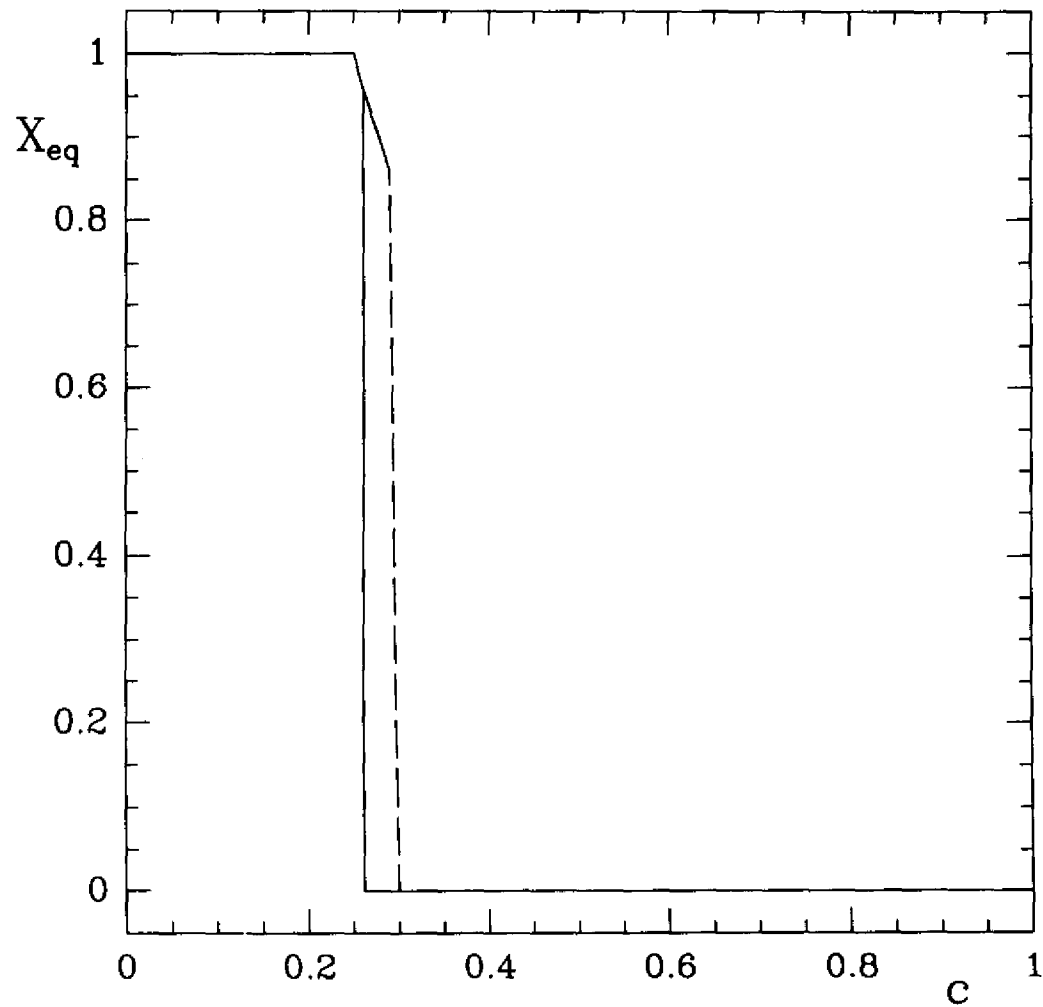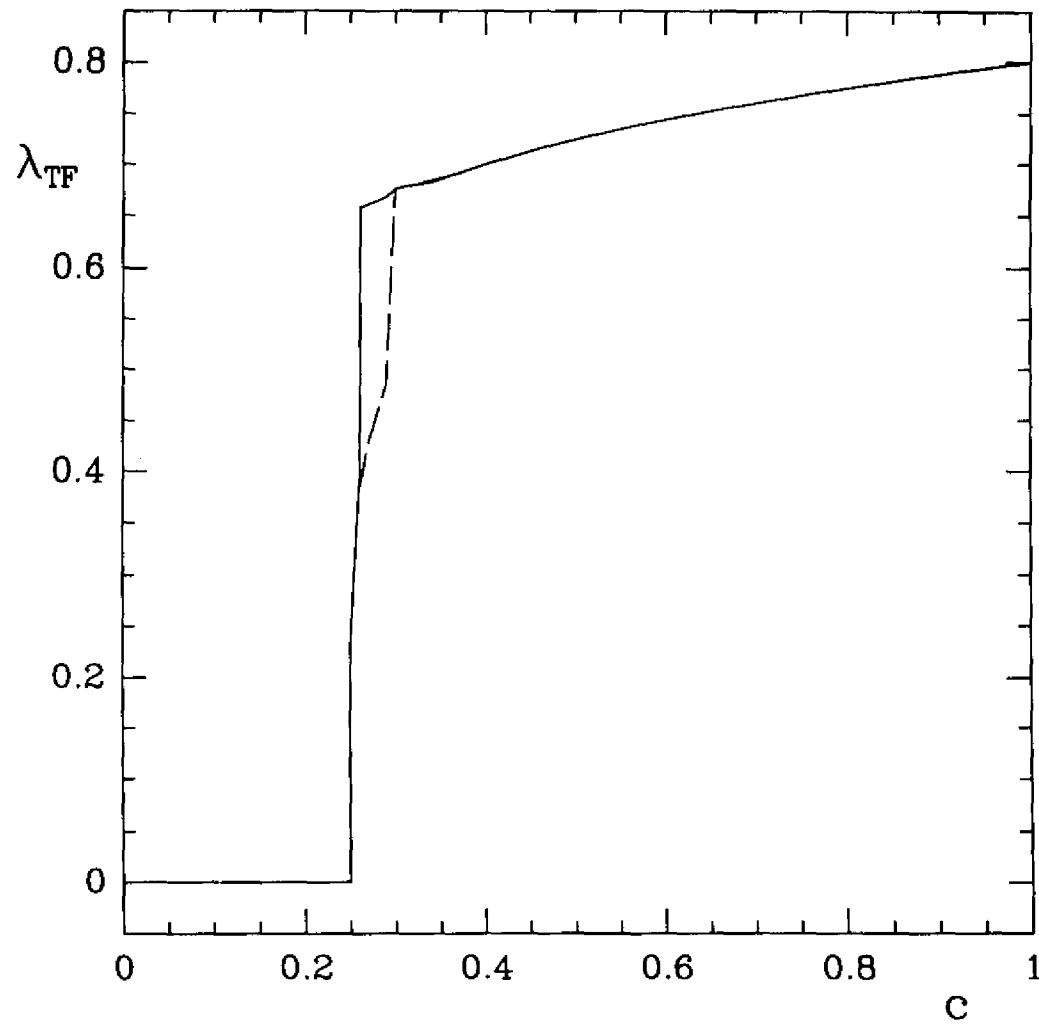**Figure 5.** - Free energy F (in kJ/mol) *versus* composition c in K-KCl at 800°C.

Fig.1

Fig.2
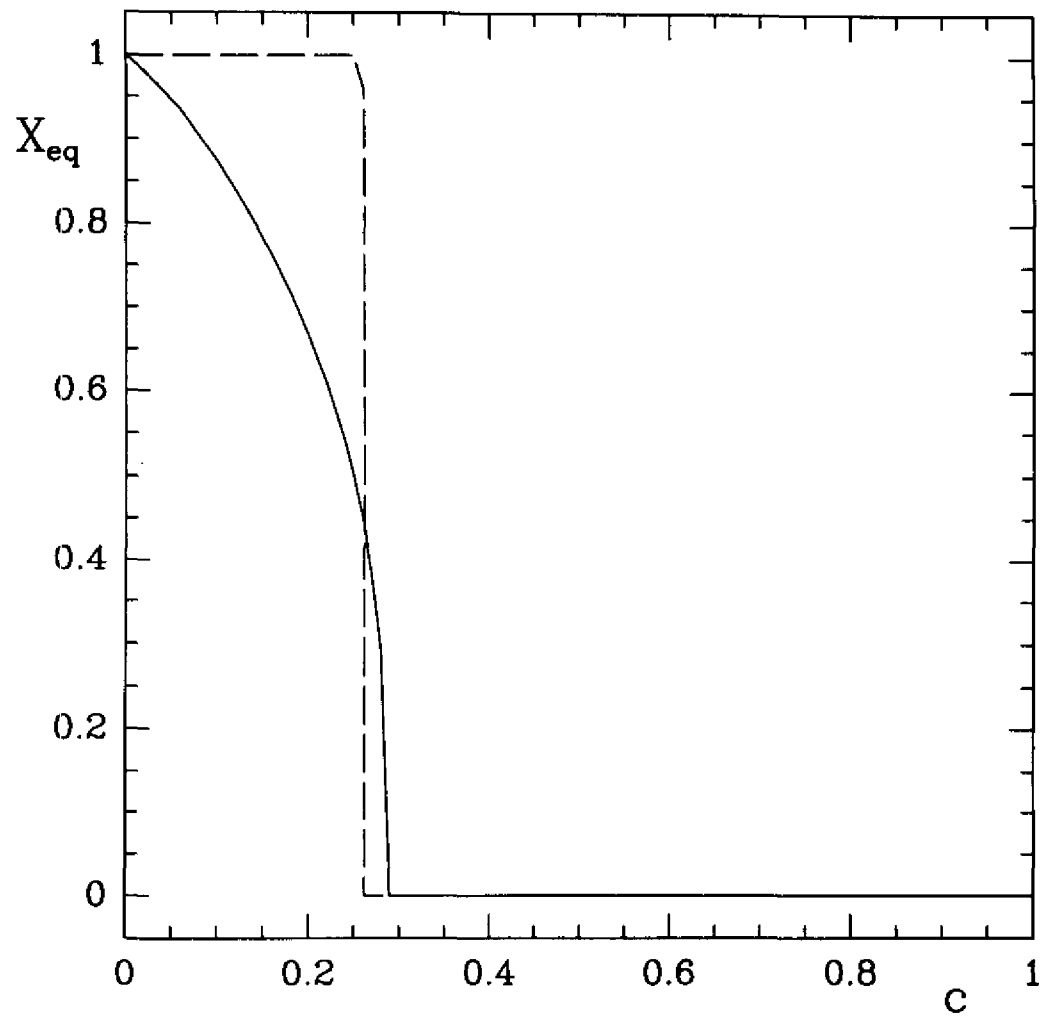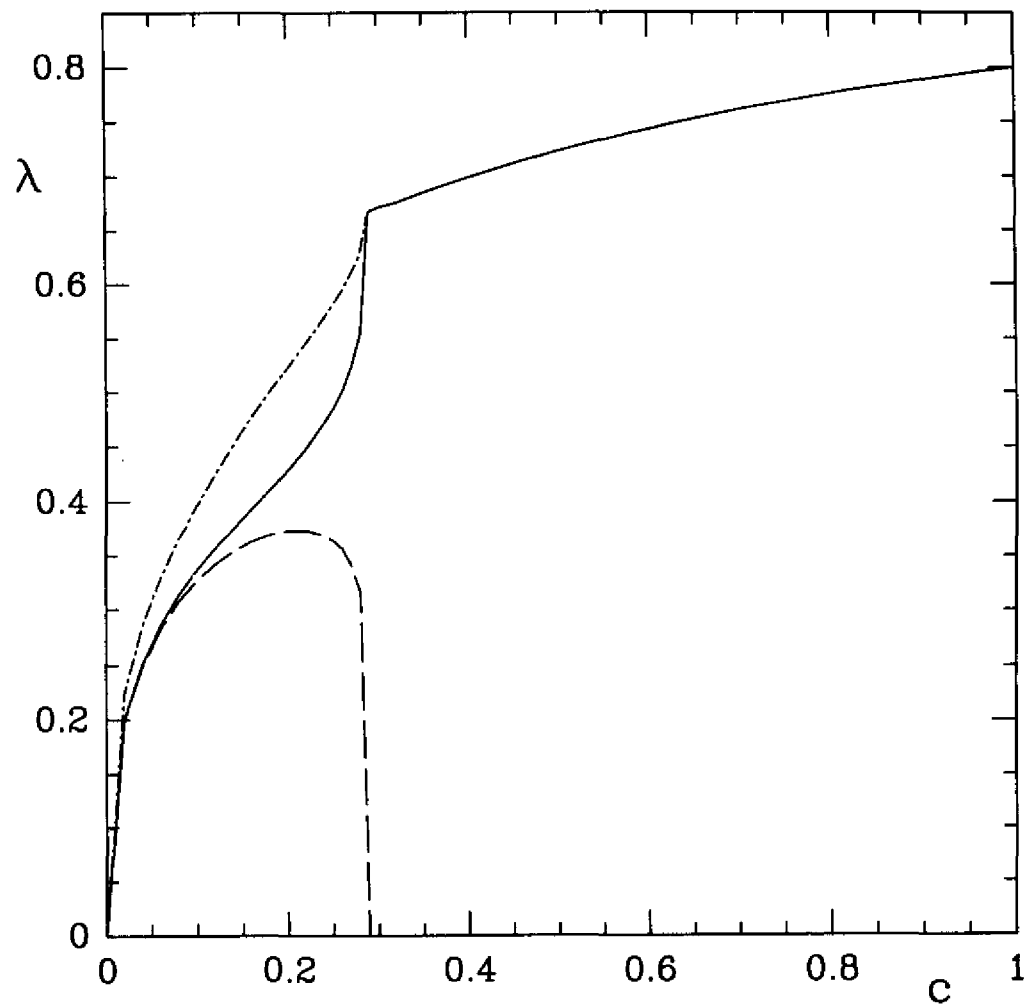
Fig.3

Fig.4

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Fig.5

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