ON
CERTAIN MANIFESTATIONS OF IONIC FORCES IN THE LIQUID AND SOLID STATE

THESIS

BY

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Introduction and Summary.

The first part of this paper was worked out in collaboration with Dr. F. Zwicky and represents a continuation of some previous work by the co-author. It is shown that the difference in thermal properties of dilute solutions against those of the pure solvent is due to the superposition of two effects: 1) A physical effect of the ion on the solvent which is manifested as an internal pressure varying from point to point in the solution. This pressure distribution is calculated for aqueous solutions of monovalent salts by an approximation theory in which the effect of the so-called ion atmosphere is estimated by means of the Debye-Huckel potential. In this as in ensuing calculations, the thermal properties of the solvent are assumed to be known. The effect of this internal pressure on the thermal coefficient of expansion and on the compressibility of dilute binary solutions is calculated and the results are found to be in satisfactory agreement with experimental values. 2) Definite evidence is obtained that the second effect determining the thermal properties of solutions is due to a chemical action of the ion on the solvent. This effect increases linearly with the molal concentration. As a result of this paper and previous work by the co-author, to which reference is given, we can say that the thermal as well as the caloric behaviour of dilute solutions is duly accounted for.

The second part of the paper was worked out in consultation with Dr. Zwicky and represents a first attempt at a rigorous treatment of the so-called mosaic structure in heteropolar crystals of the face-centered type. Certain variations from the crystal lattice of perfect symmetry are pointed out, which would lead to a decrease in potential energy. Certain energetic quantities, closely related to these variations, are calculated. An expression is obtained for the change in energy by the contraction of a 100-plane in patches, against a fixed space lattice, in terms of the end displacement (δ_e), and the number of ions in the linear patch (p). This expression is found to have a simultaneous minimum with regard to δ_e and p at a displacement and a number of ions in the patch which is in close agreement with previous phenomenological estimates. The minimum change in energy comes out positive but considerably less than the energy of thermal agitation. This then shows that at least there will be a considerable probability for patches of definite size, although with the variations here considered, these patches apparently do not represent the configuration of maximum stability. A difference in size of the patches at the surface and in the interior is also indicated by this work, a possibility which, so far as known, has not previously been pointed out in the literature.

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I. Internal Pressure in Strong electrolytes of Moderate Concentrations.

In a previous paper by one of the authors[1] the pressure distribution in a strong electrolyte of moderate concentration was calculated in connection with a detailed analysis of the specific heat of solutions. It is the purpose of the present paper to improve somewhat on this calculation, in that account will be taken of the so-called ion atmosphere[2]. As applications we shall consider the effect of this pressure distribution on the compressibility and on the thermal coefficient of expansion of aqueous solutions of monovalent salts.

As in the paper[1] already referred to, we shall choose as our starting point for the calculation of pressure the general expression for ponderomotive force on a dielectric, derived by Dallenbach[3]:

$$k_i = \rho E_i + P_k \frac{\partial E_i}{\partial x_k} + \frac{4}{5}\pi \left\{ \frac{\partial P_k}{\partial x_k} P_i + \frac{\partial P_i}{\partial x_k} P_k + \frac{\partial P_k}{\partial x_i} P_k \right\} \qquad (1)$$

where k_i is the i-component of force density, (force per unit volume), ρ is the true charge density, E_i is the i-component of electric field, and P_i is the i-component of electric polarization. The expression is to be summed over double indices.

For the derivation of Eq. (1) the assumption has to be made that, in the region considered, our medium is isotropic. The formula also holds for a crystal of the regular system. Otherwise the expression is perfectly general, and not restricted to any special functional relation between electric polarization and electric field. For small electric fields the polarization is proportional to it. For strong electric fields the polarization becomes more and more independent of the field strength due to saturation of the dielectric. Consequently, the dependency of P on E in our field will vary with the radial distance from the ion. It has been shown before[1] that a very good approximation is obtained by considering two regions, one outside a certain critical radius, r_k, and one inside. In the first region the polarization is calculated by means of the ordinary dielectric constant, whereas in the second region we use its saturation value. The latter is essentially obtained by multiplying the dipole moment by the number of molecules per cc. The critical radius, r_k, will be defined as the value of r for which the polarization as computed by the two methods is the same.

Region 1 ($r > r_k$). Let the field be some function E(r) of r which will be specified later. Then:

$$P = (D - 1)E(r)/4\pi \tag{2}$$

where D is the dielectric constant.

Referring to rectangular coordinates, we can establish the following relations for the components:

$$E = E_k x_k/r; \quad E_i = E x_i/r; \quad P = P_k x_k/r$$

$$\frac{\partial E_i}{\partial x_k} = \frac{\partial E_k}{\partial x_i} = \frac{x_i x_k}{r^2}\frac{dE}{dr} + \frac{E}{r}\left\{-\frac{x_i x_k}{r^2} + \delta_{ik}\right\}; \quad \delta_{ik} = \begin{cases} 1, & i = k \\ 0, & i \neq k \end{cases}$$

Substituting these quantities into (1) one obtains after some easy transformations:

$$|k| = |E|\left\{|\rho| + \frac{D-1}{4\pi}\cdot\left|\frac{dE}{dr}\right| + \frac{4\pi}{5}\left(\frac{D-1}{4\pi}\right)^2\left[|\operatorname{div}E| + 2\left|\frac{dE}{dr}\right|\right]\right\}$$

and since, div $(D\cdot E)=4\pi p$; div $E=4\pi p/D$

We get:

$$|k| = |E|\left\{|\rho|\left(1 + \frac{(D-1)^2}{5D}\right) + \frac{D-1}{20\pi}\left|\frac{dE}{dr}\right|(3+2D)\right\} \tag{3}$$

The absolute values can be used as shown because ρ and dE/dr always have the same sign.

For the potential of the field we shall use the value derived by Debye and Huckel.[4]

$$\psi = \frac{\nu\varepsilon}{D}\frac{e^{-xr}}{r}$$

And consequently,

$$\left.\begin{aligned} \rho &= -\frac{D}{4\pi}\nabla^2\psi = -\frac{D}{4\pi}x^2\psi \\ E &= -\frac{\partial\psi}{\partial r} = \psi\left\{x + \frac{1}{r}\right\} \\ \frac{dE}{dr} &= -\psi\left\{x^2 + \frac{2x}{r} + \frac{2}{r^2}\right\} \end{aligned}\right\} \qquad (4)$$

In these expressions ε is the elementary charge = 4.77×10^{-10} e.s.u. and ν is the valency of the ion.

$$x = \left[8\pi n(\nu\varepsilon)^2/DkT\right]^{1/2}$$

where $k=1.37 \times 10^{-16}$ ergs, (Boltzmann's constant), and n= the number of ions per cc.

Substituting the values (4) into (3), one gets after some transformations:

$$|k| = \frac{\psi^2}{20\pi}\left\{\alpha x^3 + (\alpha+2\beta)\frac{x^2}{r} + 4\beta\frac{x}{r^2} + \frac{2\beta}{r^3}\right\} \qquad (5)$$

where

$$\alpha = 3D^2+4D-2 \qquad \& \qquad \beta = 2D^2+D-3$$

The pressure is obtained by integrating k over r:

$$p = \int_r^\infty |k|\,dr = \frac{\beta(\nu\varepsilon)^2}{40\pi D^2}\,\frac{e^{-2xr}}{r^4}\left\{\frac{\alpha}{\beta}x^2r^2 + 2xr + 1\right\} \qquad (6)$$

Region 2 ($r < r_k$). The second region turns out to be comparatively small, and it is easily seen that here one may safely neglect the effect of the space charge. The error introduced in the pressure by so doing is not more than a few percent. In applications there is a more serious source of error in this region due to the uncertainty about the thermal properties of the solvent at the extremely high pressures in the neighborhood of the ion. These sources of error, however, are offset by the smallness of the region, i.e. in integrating for the thermal properties of the solution as a whole, the contribution from the region of uncertainty is small.

We shall therefore neglect the effect of space charge in this region, and write:

$$P = N\mu \; ; \quad \frac{dP}{dr} = 0 \; ; \quad E = \frac{\nu\varepsilon}{r^2} - 4\pi N\mu$$

so that,

$$|k'| = N\mu\left[2\frac{\nu\varepsilon}{r^3} - \frac{8\pi}{5}\frac{N\mu}{r}\right]$$

where N is the number of molecules per cc of solvent.

If by p_k we denote the value of the pressure at the critical radius, then,

$$\left.\begin{aligned} p &= p_k + \int_r^{r_k} |k'|\,dr = p_k + \Delta p \\ \text{where} \quad \Delta p &= N\mu\nu\varepsilon\left\{\frac{1}{r^2} - \frac{1}{r_k^2}\right\} - \frac{8\pi}{5}N^2\mu^2 \ln\frac{r_k}{r} \end{aligned}\right\} \qquad (7)$$

As we have already mentioned, the value of the critical radius is given by:

$$\frac{D-1}{4\pi}E(r_k) = \frac{D-1}{4\pi}\,\frac{\nu\varepsilon}{D}\,\frac{e^{-\kappa r_k}}{r_k}\left\{\kappa + \frac{1}{r_k}\right\} = N\mu$$

Expanding and neglecting terms of the order $(\kappa r_k)^3$ and higher, this gives:

$$r_k = \left(\frac{4\pi N\mu}{\nu\varepsilon} + \frac{\kappa^2}{2}\right)^{-\frac{1}{2}} \qquad (8)$$

In order to carry through the numerical computations we must make an assumption as to the value of μ. The dipole moment of a single water molecule can be deduced from measurements of the dielectric constant of water vapor. In this way one find $\mu_1 = 1.8 \times 10^{-18}$ e.s.u. This value, however, cannot be used on account of polymerization. In the paper 1) already referred to, it was shown by a very general consideration that the average value of μ in water must be less than 9×10^{-19} e.s.u. It is found that the best quantitative agreement with experimental results is obtained by adjusting μ to about 5×10^{-19} e.s.u.

With this value we find for aqueous solutions of monovalent salts the pressure distribution given in Table I. Γ stands for concentration in mols per 1000 grams of solvent.

These values must be further modified because our theory, while it takes account of the space charge, paradoxically so to speak, neglects the presence of the individual ions making up that space charge. It is clear that at some point in between a positive and negative ion the pressure effect must be zero, while by our theory it extends to infinity. In other words, the integration (6) should have been carried out to some finite upper limit rather than to infinity. As a somewhat arbitrary correction which, however, cannot be very far off, we propose the following: Depress the whole pressure scale by an amount equal to the pressure, p_o, at a distance r_o from the ion, and let this distance be given by the relation:

$$4\pi/3 \; r_o^3 \, \Gamma \, 2 n_o = V \qquad (9)$$

where V is the volume of a solution containing 1000 gr solvent, and n_o is the Loschmidt number = 6.06×10^{23}.

Table II gives the pressure distributions corrected as here stated. With increasing concentrations the reliability of the figures decreases. Aside from the various approximations made in this development, there are essentially two sources of error. In the first place, no account is taken of the chemical action of the ion on the solvent, an effect which so far does not permit of quantitative treatment. In the second place the effect of the ion atmosphere at high concentrations is not rigorously given by the Debye-Huckel potential. For a rigorous treatment of this effect statistical methods would have to be used 5). The mathematical difficulties of such a theory however, so far have been insurmountable.

As another, probably small, source of error, it should be mentioned that this theory does not take account of any pressure dependence of the dielectric constant. It has been shown by Roentgen 6), Falckenberg 7), and others that the pressure dependence of the dielectric constant of water is very small up to 200 kg/cm^2. No experimental data are available for pressures higher than this.

TABLE I. Pressures in kg/cm^2. Water at 20°C.

Γ	r=1A	2	3	4	5	6	7	8	9	10
0.1	76000	16000	5229	1702	522	237	117	66	38	23
0.15	76000	16000	5020	1579	474	217	106	56	32	18
0.3	75000	15330	4628	1214	406	169	78	38	-	-
0.5	74800	15036	4288	980	294	124	52	-	-	-
1.0	74580	13880	3205	687	199	-	-	-	-	-
2.0	72350	12170	2000	380	-	-	-	-	-	-

TABLE II. Pressures in kg/cm^2. Water at 20°C.

Γ	r_0	r=1A	2	3	4	5	6	7	8	9	10
0.1	12.5A	76000	16000	5220	1695	515	230	110	57	29	14
0.15	10.9	76000	16000	5010	1568	463	206	95	45	20	7
0.3	8.66	75000	15300	4604	1190	382	145	54	14	-	-
0.5	7.3	74800	14977	4247	940	253	83	11	-	-	-
1.0	5.8	74500	13800	3124	606	118	-	-	-	-	-
2.0	4.6	72200	12020	1850	227	-	-	-	-	-	-

I.B. APPLICATIONS

(a). The Thermal Coefficient of Expansion. When a solution is heated from T to T+ Δ T at constant external pressure, the internal parts of the liquid expand at variable pressures. If we consider a spherical shell of radius r and thickness dr around the ion, the expansion per degree rise in temperature will be: $d(\Delta V)/dT = dn\,dv/dT$ if $dn = 4\pi r^2 dr/v$ be the number of mols in the spherical shell.

Total expansion:

$$\frac{dV}{dT} = n\int_0^{r_0} \frac{1}{v}\,\frac{dv}{dT}\,4\pi r^2\,dr$$

and

$$\alpha_s = \frac{1}{V}\frac{dV}{dT} = \frac{3}{r_o^3}\int_0^{r_o} \frac{1}{v}\frac{dv}{dT} r^2 dr$$

Now,

$$\frac{dv}{dT} = \left(\frac{\partial v}{\partial T}\right)_p + \left(\frac{\partial v}{\partial p}\right)_T \cdot \left(\frac{d\,p(r)}{dT}\right)_r$$

So that,

$$\alpha_s = \frac{3}{r_o^3}\int_0^{r_o} \left\{ \alpha(r) - x(r)\left(\frac{d\,p(r)}{dT}\right)_r \right\} r^2 dr$$

where $\alpha(r)$ is the thermal coefficient of expansion at the pressure $p(r)$, and $X(r)$ is the compressibility at this pressure, or

$$\alpha_s - \alpha_o = \frac{3}{r_o^3}\int_0^{r_o} \left\{ \alpha(r) - \alpha_o - x(r)\left(\frac{dp(r)}{dT}\right)_r \right\} r^2 dr \qquad (10)$$

where α_o is the coefficient of expansion of the pure solvent under the given conditions of external pressure and temperature. It turns out that the isothermal expansion represented by the third member of the integrand is quite small compared with the isobar expansion $\alpha(r)$. This isothermal expansion therefore may be neglected in first approximation. The quantity (10) is to be calculated from graphical integration. The variation in thermal coefficient of expansion for pure water for pressures varying from 0 to 8000 kg/cm^2 are given by Bridgman[8)] and reproduced in Fig. 1. Beyond this upper pressure one must be satisfied by rather dubious extrapolations, but these high pressures occur only in very small regions of the solution, and contribute little to the total effect.

The pressure effect, calculated, as here outlined, is shown graphically as a function of concentration in Fig. 2. The experimental values are taken from the critical tables.[9)] The good agreement exhibited may be accidental to some extent but certainly not altogether. There is a definite qualitative agreement, and that is all we can expect, since, (by necessity), no account is taken of hydration effects in the present treatise. The experimental values for the thermal coefficient of expansion do not permit of a closer analysis of the hydration effect. In the case of the compressibility of solutions, however, we shall see definite evidence of the part played by chemical action of the ion on the solvent in determining the thermal properties of solutions.

(b). Compressibility. When the external pressure, p_0, is changed from p_0 to $p_0 + \Delta p_0$ the pressure in the interior is changed by say an amount Δp which we must determine. Consider again a spherical shell of radius r and thickness dr, containing dn mols of water. When the external pressure is increased, the change in volume of this shell will be:

$$d(\Delta V) = dn\,\Delta v = \frac{1}{v}\,\Delta v\, 4\pi r^2 dr$$

Total change:

$$\Delta V = \int_0^{r_0} \frac{\Delta v}{v}\, 4\pi r^2 dr$$

Consequently:

$$\chi_s = -\frac{1}{V}\frac{\Delta V}{\Delta p_0} = \frac{3}{r_0^3}\int_0^{r_0}\left\{-\frac{1}{v}\frac{\Delta v}{\Delta p_0}\right\} r^2 dr$$

Now, as the external pressure is increased, the radius of the shell under consideration is decreased, thereby making the internal pressure change by an amount:

$$\Delta p = \Delta p_0 + \frac{\partial p(r)}{\partial r}\Delta r$$

Hence

$$\frac{\Delta p}{\Delta p_0} = 1 + \frac{\partial p(r)}{\partial r}\frac{\Delta r}{\Delta p_0}$$

and

$$\chi_s = \frac{3}{r_0^3}\int_0^{r_0}\Bigl\{\frac{\Delta p}{\Delta p_0}\Bigl(-\frac{1}{v}\frac{\Delta v}{\Delta p}\Bigr) r^2 dr = \frac{3}{r_0^3}\int_0^{r_0}\Bigl\{1 + \frac{\partial p(r)}{\partial r}\frac{\Delta r}{\Delta p_0}\Bigr\}\chi(r)\, r^2 dr$$

An upper limit for the second term of the integrand may be obtained by the following consideration: Let $\overline{\chi(r)}$ be the compressibility of that part of the liquid which is inside a sphere of radius r around the ion. Then $\overline{\chi(r)} < \chi(r)$ And

$$\left|\frac{\Delta r}{\Delta p_0}\right| = \left|\frac{-\frac{1}{3} r \,\overline{\chi}(r)}{1 + \frac{r}{3}\frac{\partial p(r)}{\partial r}\overline{\chi}(r)}\right| < \left|\frac{-\frac{1}{3} r \,\chi(r)}{1 + \frac{r}{3}\frac{\partial p(r)}{\partial r}\chi(r)}\right|$$

By evaluating this upper limit it is seen that the second term of the integrand must be small, and that a sufficiently close approximation is obtained by using the upper limit multiplied by a correction factor χ_s/χ_0 where a first approximation value of χ_s is used.

For $\frac{\partial p(r)}{\partial r}$ we can write, to the same order of approximation,

$$\frac{\partial p(r)}{\partial r} = -4p(r)/r$$

Finally, in order to carry out the graphical integration it is more convenient to write:

$$\chi_0 - \chi_s = \frac{3}{r_0^3}\int_0^{r_0}\left\{\chi_0 - \left[1 + \frac{\partial p(r)}{\partial r}\frac{\Delta r}{\Delta p_0}\right]\chi(r)\right\} r^2 dr \tag{11}$$

The values of $\chi(r)$ are taken from Bridgman's curve, reproduced in Fig. 3.

The result of such integrations for various concentrations is plotted in Fig. 4. In the same figure we have plotted some experimental data due to Roentgen and Schneider 10). It will be seen that the experimental compressibilities are higher than those computed from the pressure effect alone. Some pertinent evidence that this may be due to hydration is given in Fig. 5. The data from which this family of curves was plotted also were taken from Roentgen and Schneider 11) and show, within the limits of experimental accuracy, that there is a linear relation between the difference in compressibility of any two binary solutions and concentration. In other words, the difference in compressibility is due to an effect which increases linearly with the number of ions of the same kind in solution. We know that as long as the supply of water molecules is sufficient each ion of the same kind will produce, qualitatively and qnantitatively, the same chemical effect on the water molecules. Therefore whatever the influence of this chemical effect on the thermal properties of the solution, we should expect a linear increase in the effect with concentration.

This linear dependency has previously been pointed out also for a caloric property of electrolytes; namely, the specific heat.1)

If, in Fig. 4, one takes the difference between the experimental curve for KCl and the theoretical curve, one obtains a linear relation up to a concentration of about 0.15 mols per liter. Beyond this point then, our approximation theory yields results which have only a qualitative, but definitely no quantitative significance. The reason for this probably is to be looked for in our method of obtaining the pressure distribution as well as in secondary hydration effects.

From this and previous work1) we can draw the conclusion that the difference in thermal and caloric properties of dilute solutions against those of the pure solvent is due to the superposition of two effects: First, a physical effect of the ion on the solvent which is predominantly manifested as an internal pressure varying from point to point in the solution. Secondly, a chemical effect of the ion on the solvent, which for dilute solutions increases linearly with the molal concentration.

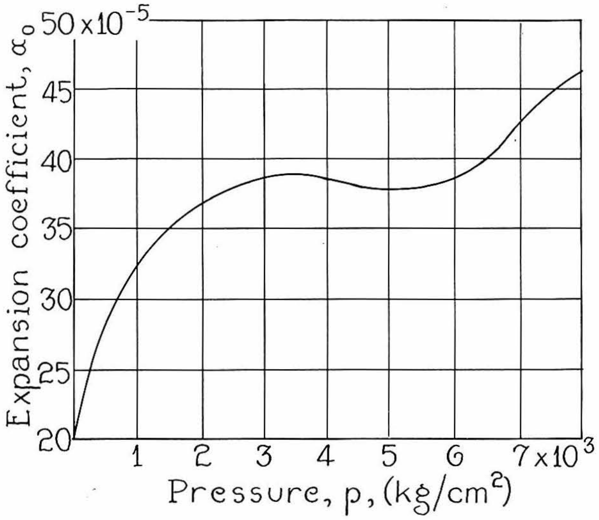

Fig.1. Coefficient of thermal expansion of water at 20° Cent.

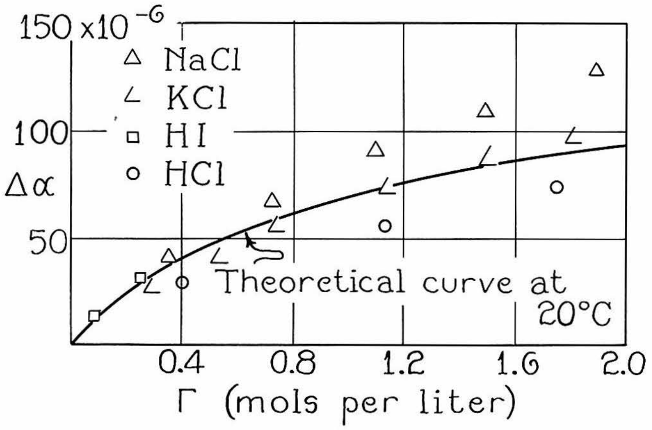

Fig. 2. $\Delta\alpha$ for solutions of NaCl, KCl, HI, HCl, at average temperature of 22.5° C as a function of concentration.

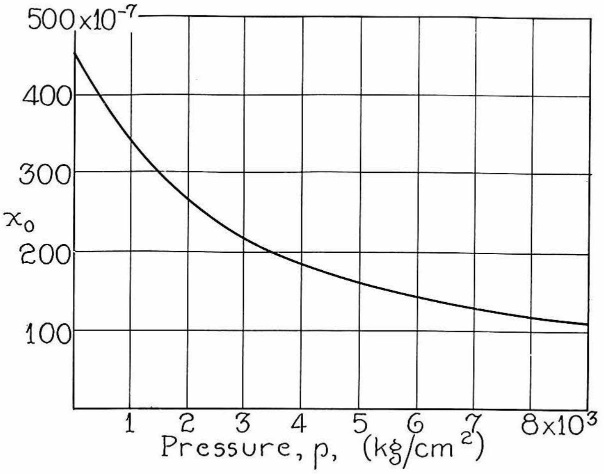

Fig 3. Compressibility of water at 20°C.
(Bridgman, 1914)

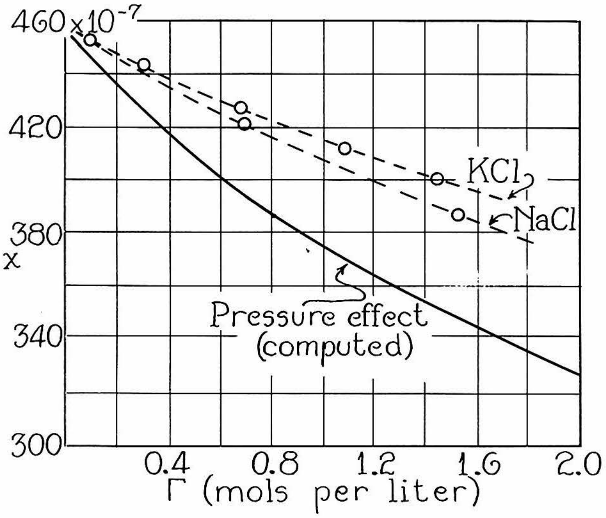

Fig4.Compressibilities of aqueous solutions at 20°C

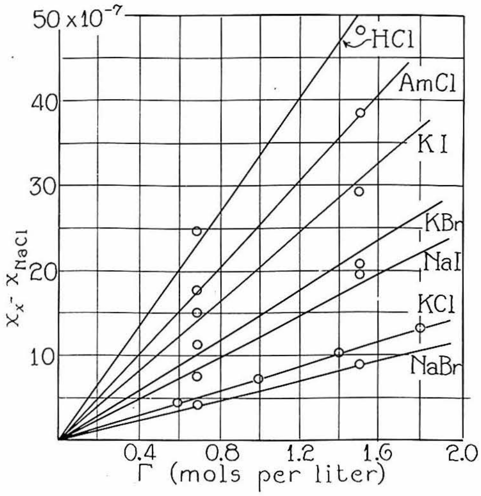

Fig. 5. Showing the linear relation between the difference in compressibility of any two binary solutions and concentration.

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3) W. Dallenbach, Phys. Zeits. 27, 632, (1926). It is doubtful whether the term ρE_i should be left in the expression, as the ions undoubtedly are somewhat accelerated by the field, and thus do not contribute by the full amount ρE_i to k_i. We have shown, however, that leaving out this term makes a difference of only about 1% in the computed pressures for aqueous solutions.
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II. On the Possibility of Mosaic Structure in Heteropolar Crystals of the Face-centered Type.

A. Descriptive.

The potential energy of two ions may be written on the form:

$$E = -\frac{e^2}{r} + \frac{A}{r^\alpha} \qquad (1)$$

Where the first term represents the potential energy due to the inverse square Coulomb forces and the second term phenomenologically stands for the energy due to the repulsive forces between ions, which are necessary for static equilibrium. A and α in general depend on the kind of ions considered 1). In the following, however, we shall confine our attention to crystals of the rock salt type and shall assume that these constants are the same for each of the three combinations of ions which occur. This greatly simplifies the calculations and is permissible in first approximation. In the case of rock salt then, the best value of α will be that corresponding to a Na-ion against a Cl-ion; namely, 9 1). With this constant fixed, and the value of the lattice constant known, the value of A may be computed from the condition that the energy shall be a minimum. With Bragg's 2) value for the lattice constant of rock salt; namely, 2.81×10^{-8}cm, the value $A = 25.8 \times 10^{-82}$ is obtained. Details of this as of ensuing computations will be found in the mathematical appendix. This calculation exemplifies the usual method of attack, whereby one assumes an infinite space lattice, perfectly symmetrical, with a lattice constant everywhere the same. It is the purpose of the present paper to investigate certain departures from this perfect symmetry which will decrease the average energy of an ion. One such variation has already been pointed out by Zwicky 3). Its reality may be easily seen by the following consideration: Consider any 100-plane in the infinite space lattice of perfect symmetry. The average energy per ion in this plane may be ascribed to two sources: 1) Energy due to the rest of the ions of this plane = Ep, and 2) Energy due to the ions outside of this plane = E_c. If we let this plane contract by an infinitessimal amount against the rest of the crystal, there will be a first order decrease in E_p, whereas, the first order change in E_c will be zero. Hence there must be a resultant decrease in energy and therefore a tendency for this plane to contract. This, of course, is due to the fact that the lattice constant of an isolated plane is smaller than that of the space lattice. In the particular case of rock salt, as shown in the appendix, the contraction amounts to 5%, and the liberation of energy by this contraction from the lattice constant of the three dimensional crystal to that of the plane amounts to 67 ergs per cm^2 of the uncontracted surface. This is of the same order of magnitude as the surface tension of the crystal which is a fact of considerable importance in the theory of sub-microscopic cracks.3)

Similarly there will be a tendency for any mixed linear point succession in the plane or in the infinite space lattice to contract. The equilibrium condition gives a lattice constant for the line which is only 87% of that of the three-dimensional crystal. The energy liberated by the contraction is 0.908×10^{-5} ergs per cm which is of the same order of magnitude as the edge energy of the crystal. In fact, it is somewhat larger4), indicating that there will be a considerable tendency for edge formation.

Similar conclusions may be drawn from a comparison of the energy of contraction of a dipole and the corner energy of the crystal.

By analogous considerations, it may be shown that certain planes and lines will have a tendency to expand. We shall, however, for the present, confine ourselves to the phenomenon of contraction.

In the case of the line or the plane respectively against the infinite space lattice, it is evident from inspection that there will be certain obstacles against the contraction of the unit as a whole. It is seen that in order to get a contraction, there must be a certain rearrangement of the ions in the lattice, or the contraction must take place in patches, or both. For the present we shall neglect the possibility of a rearrangement of the ions, and shall consider only the change in energy due to the formation of patches. This change does not necessarily have to be negative, for, superposed on this variation in any case, will be a contraction of the plane as a whole which certainly gives a considerable negative contribution. Even if the total change in energy should not be negative there might be a considerable probability for mosaic structure if the functional relation giving the change in energy in terms of the end displacement, with the number of ions (p) as a parameter, should exhibit a definite minimum at an end displacement less than the lattice constant. If, moreover, this relation should have a minimum with respect to p, we could conclude that the patches formed would have a preference as regards size.

For simplicity we shall consider only surface 100-planes, although the same considerations with only slight modifications applies also to any 100-plane in the interior. We shall start with the crystal of perfect symmetry and let the surface plane contract, keeping the rest of the ions fixed. After a certain displacement there will be an opposing force due to the rest of the crystal which will keep the ions forming the edge of the surface plane from further displacement. We shall then have a state of affairs analogous to the following simple example which permits of a rigorous solution:

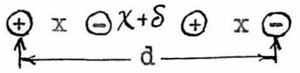

Fig.1

Consider the four ions shown in Fig.1, at first displaced at the lattice constant of the three-dimensional crystal. Keep the end ions fixed and leave the two central ions to find their equilibrium positions, which, of course, will be symmetrical. By a graphical solution of the 10th degree equation which arises, it is found that the energy is a minimum when $\delta = 0.15d$. In words, equilibrium is reached with two patches of two ions each and a considerable 'crack' in between. A similar method of approach to the problem of the contracting infinite plane would lead to an infinite number of equations and an infinite number of unknowns. It is therefore necessary to make certain simplifying assumptions.

We shall assume that the contraction takes place in patches of perfect symmetry, the contraction of two neighboring ions being everywhere $\delta_e/p-1 = \delta$ except at the edges of patches where the displacement will be δ_e. We shall next attempt to determine the first, second, and higher order changes in energy at the start of the process, and in this way obtain an expansion analogous to the Taylor series in terms of δ_e. This expansion, of course, will contain p as a parameter. The change in energy then will be expressed as follows:

$$\Delta E = f_1(p)\,\delta_e + f_2(p)\,\delta_e^2 + f_3(p)\,\delta_e^3 + \cdots \tag{2}$$

Un-fortunately this series alternates and converges somewhat slowly. It is found, however, that after the third term the higher orders may be expressed to good approximation by a simple remainder, so that we get:

$$\Delta E = f_1(p)\,\delta_e + f_2(p)\,\delta_e^2 + f_3(p)\,\delta_e^3 + R(\delta, p) \tag{3}$$

If here we impose the conditions $\dfrac{\partial \Delta E}{\partial p} = 0$ and $\dfrac{\partial \Delta E}{\partial \delta} = 0$ we obtain two equations in δ and p. This pair of equations has a solution which may be determined graphically. The value of p thus obtained checks closely with previous phenomenological estimates by Zwicky[3)] and Smekal[5)]. The change in energy corresponding to this solution is positive for the variation considered, but only about 5.5 x 10^{-15} ergs/ion, against an energy of thermal agitation of about 20 x 10^{-15} ergs/ion. Thus we have established that there will be a great probability for patches of definite size in the crystal, although with the variations considered, we have failed to show that this is a more stable configuration than the space lattice of perfect symmetry.

In order to obtain the negative change, which, as we have shown, must exist for certain variations, it may be necessary to take account of the fact that the next neighboring planes also will take part in the contraction. Or it may be necessary to consider a different kind of variation which, for example, takes account of the tendency, (which we have pointed out), of certain lines to expand. The possibility of a rearrangement of the ions in the lattice also must be considered. Although this seems to promise considerable additional complications, this will be the object of a future treatise.

B. Mathematical Appendix.

1) Computation of A.

Let the potential energy of any two ions be written on the form:

$$E = -\frac{e^2}{r} + \frac{A}{r^9} \qquad (4)$$

Then the energy of two ions in the infinite perfect crystal lattice will be:

$$E = -S_5\frac{e^2}{r} + S_6\frac{A}{r^9}$$

where $s_1 = 1.745$ and $s_2 = 6.63$ represent certain summations over the crystal which have been evaluated in the literature.6) By the minimum energy condition:

$$s_1 e^2 - 9 s_2 A / a_0^8 = 0$$

For rock salt 2), $a_0 = 2.81 \times 10^{-8}$ cm

so that

$$A = \frac{s_1 e^2 a_0^8}{9 s_2} = 25.8 \times 10^{-82} \qquad (5)$$

2) Contraction in an isolated 100-plane.

The energy of two ions in such a plane will be:

$$E = -s_3 \frac{e^2}{r} + s_4 \frac{A}{r^9}$$

where $s_3 = 1.616$ and $s_4 = 4.19$ are summations evaluated elsewhere.7)

By the equilibrium condition:

$$s_3 e^2 - \frac{9 s_4 A}{a_p^8} = 0$$

so that

$$a_0 / a_p = \left[\frac{s_2 \cdot s_3}{s_1 \cdot s_4}\right]^{1/8} = 1.049 \qquad (6)$$

Energy change by contraction:

$$\Delta E = -\frac{e^2 s_3}{a_0}\left[1.049 - 1\right] + \frac{A s_4}{a_0^9}\left[\overline{1.049}^9 - 1\right] = -67 \text{ ergs/cm}^2 \qquad (7$$

3) Contraction in an isolated mixed point succession:

Energy of two ions:

$$E = -s_5 \frac{e^2}{r} + s_6 \frac{A}{r^9}$$

where $s_5 = 2.\ln 2$ and $s_6 = 2.004$

By the equilibrium condition:

$$s_5 e^2 - \frac{9 s_6 A}{a_l^8} = 0$$

so that

$$a_0 / a_l = \left[\frac{s_2 \cdot s_5}{s_1 \cdot s_4}\right]^{1/8} = 1.129 \qquad (8)$$

Change in energy by contraction from the lattice constant of the crystal to the lattice constant of the line:

$$\Delta E = -\frac{s_5 e^2}{a_0}\left\{1.129 - 1\right\} + \frac{s_6 A}{a_0^9}\left\{\overline{1.129}^9 - 1\right\} = -0.908 \times 10^{-5} \text{ ergs/cm} \qquad (9)$$

4) Patch formation in a simple case:

Referring to Fig. 1, the energy of two ions may be expressed as follows:

$$E = -\frac{2e^2}{x_1} + \frac{2e^2}{2x_1+\delta} - \frac{e^2}{x_1+\delta} - \frac{e^2}{d} + \frac{2A}{x_1^9} + \frac{2A}{[2x_1+\delta]^9} + \frac{A}{(x_1+\delta)^9} + \frac{A}{d^9}$$

There is also the relation: $3x_1 + \delta = d = 3a_0$

The conditions for equilibrium then may be written:

$$\frac{\partial}{\partial x_1}\left\{E + \lambda(3x_1+\delta)\right\} = 0 \qquad \frac{\partial}{\partial \delta}\left\{E + \lambda(3x_1+\delta)\right\} = 0$$

Hence we get the equation:

$$e^2\left[\frac{1}{(d-\delta)^2} + \frac{1}{(2d+\delta)^2} - \frac{1}{(d+2\delta)^2}\right] = 3^{10}A\left[\frac{1}{(d-\delta)^{10}} - \frac{1}{(2d+\delta)^{10}} - \frac{1}{(d+2\delta)^{10}}\right]$$

which, when solved graphically gives: $\delta = 0.15\,d$

5) Change in energy by the formation of patches of a surface 100-plane.

The following classification will be found convenient in carrying out this calculation:

(A) According to the order of the change, or the power of . ?

(B) a) Change in energy (by contraction in patches) of linear mixed point succession.

- b) Change in energy by patch contraction of isolated 100-plane.
- c) Change in energy of ions in line due to the rest of the ions in the plane defined by that line.
- d) Change in energy of ions in line due to the rest of the ions of the crystal except as computed under c).

(C) Change in energy due to polarization.

6) Second order change in energy.

The first order effects vanish throughout; so we shall proceed with the second order change:

(a) Linear mixed point succession:

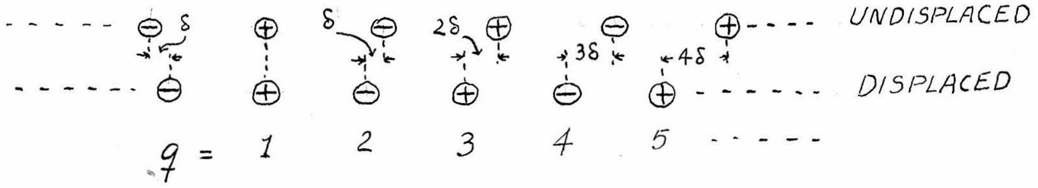

Fig. 2.

Referring to Fig. 2 we can write the general Coulomb energy of the contracted line gitter:

$$E^- = \sum_{-\infty}^{\infty}{}' (-1)^n \frac{e^2}{|n|a - k\delta} \qquad [n \neq 0] \tag{10}$$

where k = $k_q(n,p)$ is a function of the periodicity p, (or number of ions in the patch), and also of the serial number q of the particular ion considered. The average second order change in energy per ion due to a displacement δ of periodicity p, therefore, will be:

$$\Delta E^{(2)} = -\frac{1}{2}\frac{e^2\delta^2}{a^3}\sum_{n=-\infty}^{\infty}(-1)^{n+1}\frac{\frac{1}{p}\sum_{q=1}^{p} k_q^2}{|n|^3} \tag{11}$$

$K_p(n) = \frac{1}{p}\sum_{1}^{p} k_q^2$ turns out to be an even function of n, so we can write:

$$\overline{\Delta E}^{(2)} = -\frac{e^2\delta^2}{a^3}\sum_{n=1}^{\infty}(-1)^{n+1}\frac{K_p(n)}{n^3}$$

where it is easily seen that: $K_p(n) = r[n/p](p - r[n/p])$ (12)

(The symbol r(n/p) stands for remainder in n/p)

or with the abbreviation: $\sum_{1}^{\infty}(-1)^{n+1}\frac{K_p(n)}{n^3} = S_p$

$$\overline{\Delta E}^{(2)} = -S_p\frac{e^2\delta^2}{a^3}$$

S_p has been evaluated by direct summation for a number of different values of p. By a somewhat different method of attack, however, (as exemplified under the computation of polarization energy), the following summation formula for S_p was obtained:

$$p\,S_p = \frac{1}{2}\sum_{1}^{p}(-1)^s(p-s)\,s^2\,U_{s+1} \tag{13}$$

where $$U_{s+1} = -\frac{1}{p^3}\left\{\psi''\left(\frac{s}{p}+1\right)+\psi''\left(2-\frac{s}{p}\right)-2\left[\left(\frac{p}{s}\right)^3+\left(\frac{p}{p-s}\right)^3\right]\right\} \qquad \Big)\,p \text{ even} \quad (14$$

and $$U_{s+1} = -\frac{1}{(2p)^3}\left\{\psi''\left(\frac{s}{2p}+1\right)+\psi''\left(2-\frac{s}{2p}\right)-\psi''\left(\frac{s}{2p}+\frac{3}{2}\right)-\psi''\left(\frac{3}{2}-\frac{s}{2p}\right)\right.$$
$$\left.-2\left[\left(\frac{2p}{s}\right)^3+\left(\frac{2p}{2p-s}\right)^3-\left(\frac{2p}{s+p}\right)^3-\left(\frac{2p}{p-s}\right)^3\right]\right\} \qquad p \text{ odd} \quad (15$$

Here $\psi''(x+1) = \frac{d^2}{dx^2}\psi(x+1)$ 8) which will be found tabulated in the literature.

The above expression for S_p may be further simplified if one observes that:

$$U_{s+1} = U_{p-s+1} \quad ---- \; p \text{ even}$$

$$U_{s+1} = -U_{p-s+1} \quad ----- \; p \text{ odd}$$

This gives:

$$S_p = \frac{1}{2}\left\{(-1)^{p/2}\frac{p^2}{8}U_{p/2+1} + \sum_{1}^{p/2-1}(-1)^s s(p-s)U_{s+1}\right\} \quad p \text{ even} \qquad (16)$$

$$S_p = \frac{1}{2}\sum_{1}^{\frac{p-1}{2}}(-1)^s s(p-s)U_{s+1} \quad --------- \; p \text{ odd} \qquad (17)$$

For reasonably large values of $p(p > 10)$, it is found from this, that the second order change in the Coulomb energy may be represented as follows:

$$\overline{\Delta E}^{(2)-} = -\frac{e^2\delta^2}{a^3}\left[0.823p - 0.71\right] \qquad (18)$$

The second order change in the energy of repulsion similarly may be written: $$\overline{\Delta E}^{(2)+} = \frac{1}{2}\,\frac{A\alpha(\alpha+1)}{a^{\alpha+2}}\,\delta^2\sum_{1}^{\infty}\frac{K_p(n)}{n^{\alpha+2}} = 1.31\,\frac{e^2\delta^2}{a^3}\left(\frac{a_0}{a}\right)^8(p-1) \qquad (19)$$

? 1.034

(b) Contraction of isolated 100-plane.

The energy of an average ion in the plane may be thought of as due to the following sources: 1) Energy due to two intersecting perpendicular lines. These contribute equally by the amount computed under (a). 2) Energy due to the rest of the ions of the plane. This will be given by:

$$E = \frac{A}{[(la-k_1\delta)^2+(ma-k_2\delta)^2]^{\frac{\alpha}{2}}} = \frac{A}{[(la)^2+(ma)^2]^{\frac{\alpha}{2}}} \cdot \frac{1}{\left[1-\frac{2a\delta[lk_1+mk_2]-\delta^2[k_1^2+k_2^2]}{(la)^2+(ma)^2}\right]^{\alpha/2}} \qquad (20)$$

Noticing that cross-products of k_1 and k_2 must vanish in the summation, we can write the second order change:

$$\Delta E^{(2)}_{l,m} = \frac{\alpha p^2\delta^2}{2\,a^{\alpha+2}}\,\frac{A}{[l^2+m^2]^{\frac{\alpha+4}{2}}}\left[r[l/p]\{p-r[l/p]\}[(\alpha+1)l^2-m^2]+r[m/p]\{p-r[m/p]\}[(\alpha+1)m^2-l^2]\right]$$

This expression is symmetrical in m and l, so that in the summation the two members of the bracket contribute equally. Hence, we get for the second order change in the Coulomb energy:

$$\overline{\Delta_2^-} = \frac{2e^2\delta^2}{a^3}\sum_{m=1}^{\infty}\sum_{l=1}^{\infty}(-1)^{l+m}\,\frac{r[l/p](p-r[l/p])\{2l^2-m^2\}}{[l^2+m^2]^{5/2}} \qquad (21)$$

And for the second order change in the energy of repulsion:

$$\overline{\Delta_2^+} = \frac{18A\delta^2}{a^{11}}\sum_{m=1}^{\infty}\sum_{l=1}^{\infty}\frac{r[l/p]\{p-r[l/p]\}[10l^2-m^2]}{[l^2+m^2]^{13/2}} \qquad (22)$$

These series were evaluated by direct summation to fair accuracy. The result for $p > 10$:

$$\overline{\Delta_2^-} = \left(\frac{2p}{17}+0.106\right)\frac{\delta^2e^2}{a^3} \qquad (23)$$

$$\overline{\Delta_2^+} = 1.84(p-1)\frac{\delta^2A}{a^{11}} = 0.053(p-1)\frac{\delta^2e^2}{a^3}\left(\frac{a_0}{a}\right)^8 \qquad (24)$$

(c) <u>Change in energy of ions of contracting line due to the rest of the ions in the plane defined by this line.</u>

Referring to Fig. 3, we can write the energy of an ion

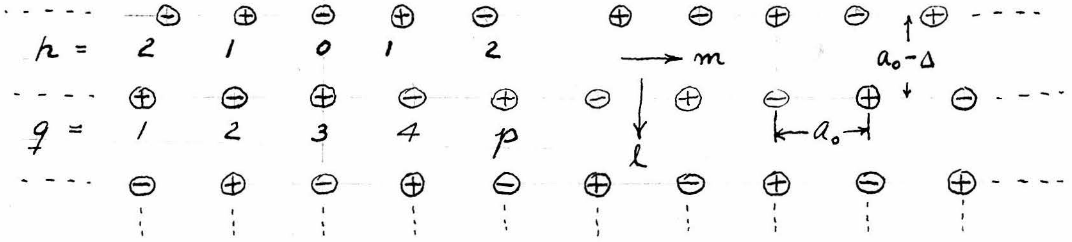

Fig.3.

in the boundary line w.r. to the rest of the ions in the plane:

$$E^{k}_{l,m} = \frac{A}{\left[(la)^2 + (ma - k\delta)^2\right]^{\alpha/2}} \tag{25}$$

where $h = h_q(m)$

From this the second order change in energy is easily seen to be:

$$\overline{\Delta}_2 = \frac{\alpha A \delta^2}{a^{\alpha+2}} \left\{ \sum_{l=1}^{\infty} \sum_{m=1}^{\infty} \frac{1}{p} \sum_{q=1}^{p} h^2 \frac{(\alpha+1)m^2 - l^2}{[l^2+m^2]^{\frac{\alpha+4}{2}}} - \frac{1}{2} \sum_{l=1}^{\infty} \frac{1}{p} \sum_{q=1}^{p} h^2 \frac{1}{l^{\alpha+2}} \right\} \tag{26}$$

From Fig. 3, it appears that:

$$\frac{1}{p} \sum_{q=1}^{p} h^2 = \frac{p^2-1}{12} \tag{27}$$

Hence:

$$\overline{\Delta}_2 = \frac{\alpha A \delta^2}{a^{\alpha+2}} \frac{p^2-1}{12} \left[\sum_{1}^{\infty} \sum_{1}^{\infty} \frac{(\alpha+1)m^2 - l^2}{[l^2+m^2]^{\frac{\alpha+4}{2}}} - \frac{1}{2} \sum_{l=1}^{\infty} \frac{1}{l^{\alpha+2}} \right] \tag{28}$$

which by adjustment of the constants gives:

Change in Coulomb energy: $\overline{\Delta}_2^{-} = \dfrac{e^2\delta^2(p^2-1)}{12a^3} \left\{ S_1 - \tfrac{1}{2} S_2 \right\}$ (29)

Change in repulsive energy: $\overline{\Delta}_2^{+} = \dfrac{9A\delta^2(p^2-1)}{12a^{11}} \left\{ S_3 - \tfrac{1}{2} S_4 \right\}$ (30)

where $S_1 = \sum_1^{\infty} \sum_1^{\infty} (-1)^{l+m} \dfrac{2m^2 - l^2}{[l^2+m^2]^{5/2}} = 0.12$; $S_3 = \sum_1^{\infty} \sum_1^{\infty} \dfrac{10m^2 - l^2}{(l^2+m^2)^{13/2}} = .1$

$S_2 = \sum_1^{\infty} (-1)^l \dfrac{1}{l^3} = -\dfrac{3}{4} \dfrac{\pi^3}{25.7946\ldots} = -0.902$; $S_4 = \sum_1^{\infty} \dfrac{1}{l^{11}} = 1.0005$

These results still must be corrected for the Lennard-Jones[1] contraction perpendicular to the surface. That is, in the terms containing $l = 1$, this must be replaced by 0.95. As a final result, we obtain:

$$\overline{\Delta E}_2 = (p^2-1) \frac{e^2\delta^2}{a^3} \left\{ .053 - .015\left(\frac{a_0}{a}\right)^8 \right\} \tag{31}$$

(d) Change of energy of ions in line due to the rest of the ions of the space lattice except as computed under (c).

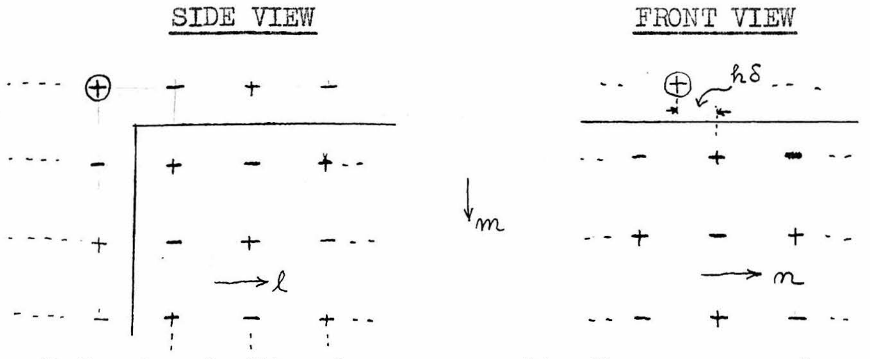

Fig. 4.

Referring to Fig. 4, we may write the energy under consideration as follows:

$$E_{l,m,n} = \frac{A}{\left[(la)^2+(ma)^2+(na-h\delta)^2\right]^{\frac{\alpha}{2}}} \tag{32}$$

Where the limits of variability of l,m, and n are:

$l = -\infty \cdots\cdots\cdots +\infty \quad l \neq 0$

$m = 1 \cdots\cdots\cdots +\infty$

$n = -\infty \cdots 0 \cdots +\infty$

From this, we can write the second order change in energy as follows:

Repulsion: $$\frac{9(p^2-1)}{12}\;\frac{\delta^2 A}{a^{11}}\left[2S_1 - S_2\right] \tag{33}$$

Coulomb: $$\frac{p^2-1}{12}\;\frac{\delta^2 e^2}{a^3}\left[2S_3 - S_4\right] \tag{34}$$

where $$S_1 = \sum_1^\infty\sum_1^\infty\sum_1^\infty \frac{10n^2-l^2-m^2}{\left[l^2+m^2+n^2\right]^{13/2}} = 0.0067$$

$$S_2 = \sum_1^\infty\sum_1^\infty \frac{1}{\left[l^2+m^2\right]^{11/2}} = 0.0224$$

$$S_3 = \sum_1^\infty\sum_1^\infty\sum_1^\infty (-1)^{l+m+n}\frac{2n^2-l^2-m^2}{\left[l^2+m^2+n^2\right]^{5/2}} = -0.033$$

$$S_4 = \sum_1^\infty\sum_1^\infty \frac{(-1)^{l+m}}{\left[l^2+m^2\right]^{3/2}} = 0.241$$

S_1, S_2, and S_3 were evaluated by direct summation. S_4, on the other hand, was derived from a known series by a method which will be reproduced below. With the correction for the Lennard-Jones contraction of the terms containing m = 1, the final result is:

$$\overline{\Delta E_2} = -.0266\,(p^2-1)\,\frac{\delta^2 e^2}{a^3} \tag{35}$$

(d') Derivation of the series S_4

The value of the series S_0 is given in the literature 9).

It is: $$S_0 = \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty}\frac{1}{(m^2+l^2)^{3/2}} = 9.0336 \qquad \{|m|+|l| \neq 0\}$$

Then: $$S_0 = 4\sum_1^{\infty}\sum_1^{\infty}\frac{1}{[m^2+l^2]^{3/2}} + 4\sum_1^{\infty}\frac{1}{l^3} = 4\Sigma_1 + 4A_0$$

Where: $$A_0 = \frac{\pi^3}{25.7946\ldots}$$

Hence: $$\Sigma_1 = \frac{S_0}{4} - A_0$$

Now: $$S_4 = \sum_1^{\infty}\sum_1^{\infty}\frac{(-1)^{m+l}}{[m^2+l^2]^{3/2}} = \Sigma_2 - \Sigma_3$$

where: $$\Sigma_2 = \sum_1^{\infty}\sum_1^{\infty}\frac{1}{[m^2+l^2]^{3/2}} \quad \text{with } m+l \text{ even}$$

and $$\Sigma_3 = \sum_1^{\infty}\sum_1^{\infty}\frac{1}{[m^2+l^2]^{3/2}} \quad \text{'' \quad '' odd}$$

Now: $$\Sigma_1 = \Sigma_2 + \Sigma_3$$

So that: $$S_4 + \Sigma_1 = 2\Sigma_2 = 2\left\{\frac{1}{4}\,2^{-3/2}S_0 - \sum_1^{\infty}\frac{1}{(2n)^3}\right\} = \frac{1}{4}\left[\frac{S_0}{\sqrt{2}} - A_0\right]$$

Hence: $$S_4 = \frac{1}{4}\left[\frac{S_0}{\sqrt{2}} - A_0\right] - \Sigma_1 = \frac{1}{4}\left[\left\{\frac{1}{\sqrt{2}} - 1\right\}S_0 + 3A_0\right] = 0.241$$

(e) Second order effects summarized.

The total change in energy due to Coulomb and repulsive forces now may be written: $(a = a_0)$

$$\Delta \overline{E}^{(2)} = 1.14(p-1)\frac{\delta^2 e^2}{a^3} + 0.0114(p^2-1)\frac{\delta^2 e^2}{a^3} \tag{36}$$

For future use it is more convenient to express this in terms of the end displacement $\delta_e = \delta\,(p-1)/a$. Hence:

$$\overline{\Delta E}^{(2)} = \frac{\delta_e^2 e^2}{a}\left\{\frac{1.14}{p-1} + 0.0114\frac{p+1}{p-1}\right\} \tag{37}$$

(f) Some general remarks about the second order change.

At this stage of the calculations may we interrupt to call attention to the physical meaning of the results obtained so far. The fact that the first order change in energy is zero and the second order positive must be taken to mean that at the start of the process of contraction there is no tendency for patch formation, since the energy is a minimum against the variation. To see whether the energy does not become negative or does not possess definite minima at finite end displacements we shall proceed to calculate the higher order changes in energy. First, however, may we also call attention to the fact that the contribution of the space lattice to the change in energy (ΔE_c) contains p to a higher power than the contribution of the plane (ΔE_p). This indicates that the limit to the size of the patches will be set by ΔE_c, which again tells us that there is going to be a difference in size between the patches in the interior and at the surface, since ΔE_c, aside from the effect of the Lennard-Jones contraction, is twice as large in the former case as in the latter.

7) <u>Third Order changes in energy</u>.

a) Linear mixed point succession.

The change in energy will be:

Coulomb: $$\frac{e^2\delta^3}{a^4}\sum_1^\infty \frac{\frac{1}{p}\sum_1^p k^3}{n^4}(-1)^n \qquad (38)$$

Repulsion: $$\frac{9\cdot 10\cdot 11}{2\cdot 3}\frac{\delta^3 A}{a^{12}}\sum_1^\infty \frac{\frac{1}{p}\sum_1^p k^3}{n^{12}} \qquad (39)$$

where $$\frac{1}{p}\sum_1^p k^3 = -r[n/p]\{p - r[n/p]\}\{p - 2r[n/p]\} \qquad (40)$$

For $p > 10$ this gives to fair approximation:

Coulomb: $$0.91(p-1)(p-2)\frac{e^2\delta^3}{a^4} \qquad (41)$$

Repulsion: $$-4.81(p-1)(p-2)\frac{e^2\delta^3}{a^4} \qquad (42)$$

b) <u>Contraction of isolated 100-plane</u>.

The change in energy except as computed under (a) will be:

Coulomb: $$\frac{6e^2\delta^3}{a^4}\sum_1^\infty\sum_1^\infty \frac{\frac{1}{p}\sum_1^p k_l^3\cdot l\{\frac{2}{3}l^2 - m^2\}}{[l^2+m^2]^{7/2}}(-1)^{m+l} \qquad (43)$$

Repulsion: $$\frac{2\cdot 9\cdot 11\cdot A\delta^3}{a^{12}}\sum_1^\infty\sum_1^\infty \frac{\frac{1}{p}\sum_1^p k_l^3\cdot l\{\frac{10}{3}l^2 - m^2\}}{[l^2+m^2]^{15/2}} \qquad (44)$$

For $p > 10$ this gives to fair approximation:

Coulomb: $$0.223(p-1)(p-2)\frac{e^2\delta^3}{a^4} \qquad (45)$$

Repulsion: $$-0.08(p-1)(p-2)\frac{e^2\delta^3}{a^4} \qquad (46)$$

c) <u>Third order effect against crystal</u>.

It is evident that this effect must vanish throughout.

d) <u>Total third order change</u>:

$$\overline{\Delta E_3} = -7.66(p-1)(p-2)\frac{e^2\delta^3}{a^4} \qquad (47)$$

Or, in terms of the end displacement:

$$\overline{\Delta E_3} = -7.66\frac{p-2}{(p-1)^2}\frac{e^2\delta_e^3}{a} \qquad (48)$$

8) Fourth and higher order changes in energy.

The 4th order Coulomb contribution of two intersecting perpendicular linear mixed point successions will be:

$$2\ \frac{\delta^4 e^2}{a^5}\sum_1^{\infty}(-1)^n \frac{\frac{1}{p}\sum_1^{p} k^4}{n^5} \tag{49}$$

For p > 10 this may be expressed approximately as:

$$\overline{\Delta E_4^-} = -\frac{2(p-1)^4}{p}\,\frac{\delta^4 e^2}{a^5} \tag{50}$$

or in terms of the end displacement:

$$\overline{\Delta E_4}^- = -\frac{2}{p}\,\frac{\delta_e^4 e^2}{a} \tag{51}$$

In first approximation, this may be considered as the total Coulomb contribution to the fourth order change. The actual value will be a few per cent smaller than this. An estimate of the higher order change in Coulomb energy then may be obtained as follows:

$$\overline{\Delta E}^- = -\frac{2e^2}{pa}\left\{\frac{1}{1+\delta_e} - 1 + \delta_e - \delta_e^2 + \delta_e^3\right\} \tag{52}$$

The energy of repulsion may be represented to fair approximation by the first term in the expansion, for the fourth and higher orders. That is:

$$\frac{9\cdot(9+1)\cdot\cdots\cdot(9+\gamma-1)}{\gamma!}\ \frac{A}{p}\,(-1)^\gamma\,\frac{(p-1)^\gamma}{a^{9+\gamma}}\,\delta^\gamma \tag{53}$$

which will be seen to represent a general term in the binominal expansion of:

$$\frac{1}{p}\,\frac{A}{a^9}\,\frac{1}{(1+\delta_e)^9} \tag{54}$$

Consequently, the fourth and higher orders of the energy of repulsion may be written:

$$\overline{\Delta E}^+ = \frac{0.0583}{p}\,\frac{e^2}{a}\left\{\frac{1}{(1+\delta_e)^9} - 1 + 9\,\delta_e - \frac{9\cdot 10}{2}\delta_e^2 + \frac{9\cdot 10\cdot 11}{2\cdot 3}\,\delta_e^3\right\} \tag{55}$$

which may be taken to mean that these higher orders arise entirely from the change in energy of the ions forming the boundaries of the patch.

9) Energy of polarization.

We shall first consider the energy of polarization created by patch contraction of a linear mixed point succession although the result of this calculation will not be directly applicable to the plane due to the vectorial nature of the field strength. For this purpose we shall consider the displaced point succession as a number of interposed linear gitters, the number of such gitters being p, and the gitter constant of these gitters pa. If p is odd, it is seen that these elementary point successions will be mixed, whereas, if p is even, all the charges making up the elementary linear gitter will have the same sign.

The following notation will be used:

F_{rs}= field strength at ion #r due to the elementary gitter of which s is a member.

We can then write the following symmetry relations:

1) $F_{qq} = 0$

2) $F_{qs} = F_{sq}$ if $q-s = \pm 2n-1$

3) $F_{qs} = -F_{sq}$ if $q-s = \pm 2n$

4) $F_{qs} = F_{rt}$ if $q-r = s-t = \pm 2n$

5) $F_{qs} = -F_{rt}$ if $q-r = s-t = \pm 2n-1$

For $s > q$ we obtain from this

$$F_{qs}=(-1)^{q-1} F_{1,\, s-q+1}$$

For $s < q$, we obtain:

$$F_{qs}=(-1)^{q} F_{1,\, q-s+1}$$

Hence we can write for - - - $\sum_{s=1}^{p} F_{qs}$

$$\sum_{s=1}^{p} F_{qs} = (-1)^{q+1} \sum_{r=q+1}^{p-q+1} (-1)^{r} F_{r1} \quad \text{- - - - - - - - - - - - - - - - if } q \leq p/2$$

$$= 0 \quad \text{- - - - - - - - - - - - - - - if } q = (p+1)/2$$

$$= (-1)^{q} \sum_{p-q+2}^{q} (-1)^{r} F_{r1} \quad \text{- - - - - - - - - - - if } q > (p+1)/2$$

Only the first of these relations interest us since if the field strength is known at the first half of the ions the field strength at the remainder follows by symmetry.

Now we can write:

$$F_{r+1,1} = -\frac{dV}{dx}\Big]_{x=r(a-\delta)} = -\frac{dV}{dx}\Big]_{x=ra} + r\delta\,\frac{d^2V}{dx^2}\Big]_{x=ra} - \cdots \tag{56}$$

where 6)

$$V_{odd} = -\frac{e}{2pa}\Big[\psi\Big(\frac{x}{2pa}+1\Big) + \psi\Big(2-\frac{x}{2pa}\Big) - \psi\Big(\frac{x}{2pa}+\frac{3}{2}\Big) - \psi\Big(\frac{3}{2}-\frac{x}{2pa}\Big)$$

p odd

$$- \frac{2pa}{x} - \frac{2pa}{2pa-x} + \frac{2pa}{x+pa} + \frac{2pa}{pa-x}\Big] \tag{57}$$

and
p even

$$V_{even} = -\frac{e}{pa}\Big[\psi\Big(\frac{x}{p}+1\Big) + \psi\Big(2-\frac{x}{p}\Big) - \Big[\frac{p}{x} + \frac{p}{p-x}\Big]\Big] \tag{58}$$

So that for p ~~odd~~ even:

$$\Delta E_q = -\frac{\alpha}{2}\Big[\sum_s F_{qs}\Big]^2 = -\frac{1}{2}\,\frac{\alpha\delta^2 p^2}{a^6}\Big\{\sum_q^{p/2}(-1)^r U_{r+1} - \frac{1}{2}(-1)^{p/2}U_{p/2+1}\Big\}^2$$ (See eq.14)

and for p ~~even~~ odd:

$$\Delta E_q = -\frac{\alpha}{2}\Big[\sum_s F_{qs}\Big]^2 = -\frac{1}{2}\,\frac{\alpha\delta^2 p^2}{a^6}\Big\{\sum_q^{\frac{p-1}{2}}(-1)^r U_{r+1}\Big\}^2$$ (See eq. 15)

So that the change in energy by polarization becomes:

p odd

$$\Delta E = -\frac{\alpha\delta^2 p}{a^6}\sum_{q=1}^{\frac{p-1}{2}}\Big\{\sum_{r=q}^{\frac{p-1}{2}}(-1)^r U_{r+1}\Big\}^2 \tag{59}$$

p even

$$\Delta E = -\frac{\alpha\delta^2 p}{a^6}\sum_{q=1}^{p/2}\Big\{\sum_q^{p/2}(-1)^r U_{r+1} - \frac{1}{2}(-1)^{p/2}U_{p/2+1}\Big\}^2 \tag{60}$$

where

$$\alpha = \frac{1}{2}\big\{\alpha_{Na} + \alpha_{Cl}\big\} \tag{61}$$

These expressions reach the same asymptotic value. The negative change, however, in general is higher for an even number of ions in the patch than for an odd number.

With Born's 10) values for the polarizabilities the asymptotic change in energy becomes:

$$\Delta E = -3.3\,\frac{e^2}{a^6}\,p\,\alpha\,\delta^2 = -\,0.245\,p\,\frac{e^2\delta^2}{a^3} \tag{62}$$

10) <u>Second order polarization in plane</u>.

No convenient general expression has as yet been developed for the potential due to a plane gitter, so we shall resort to the method of direct expansion.

With our previous notation, the x-component of the field at ion #q becomes:

$$\Delta X^q = -\sum_{l=-\infty}^{\infty}(-1)^l\frac{2e\delta k_1}{a^3 l^3} + \sum_{-\infty}^{\infty}\frac{e\delta}{a^3}\,\frac{k_1(m^2-2l^2)-3k_2 lm}{[l^2+m^2]^{5/2}}(-1)^{l+m} \tag{63}$$

The first summation has been worked out under (9), in fact:

$$\Delta X_0^q = \sum_{-\infty}^{\infty} -\frac{2\delta e\,k_1(-1)^l}{a^3\,l^3} = (-1)^q\,\frac{\delta p e}{a^3}\left\{\sum_{q}^{p/2}(-1)^r U_{r+1} + \frac{1}{2}(-1)^{p/2+1}U_{p/2+1}\right\} \tag{64}$$

(p even)

so that: $$\Delta X^q = \Delta X_0^q + \Delta X_1^q \tag{65}$$

where $$\Delta X_1^q = \frac{\delta e}{a^3}\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty}\frac{k_1(m^2-2l^2)}{[l^2+m^2]^{5/2}}(-1)^{l+m} \tag{66}$$

For p large the expression gives approximately:

$$\Delta X_1^1 = \frac{2p\,\delta e}{a^3}\sum_1^{\infty}\sum_1^{\infty}(-1)^{l+m}\frac{m^2-2l^2}{[l^2+m^2]^{5/2}} \tag{67}$$

$$\Delta X_1^2 = \Delta X_1^1 - \frac{2p\,\delta e}{a^3}\sum_1^{\infty}(-1)^{m+1}\frac{(m^2-2)}{[1^2+m^2]^{5/2}} \tag{68}$$

etc.

These summations have been worked out previously.

The result of the calculations follows:

$$\overline{\Delta E} = p\,\frac{\alpha}{2}\left\{\sum_1^p \overline{\Delta X^{q}}^2 + \overline{\Delta Y^{q}}^2\right\} = 4.94\,\alpha\,\frac{\delta^2 e^2}{a^6}\,p$$

$$= .366\,\frac{\delta^2 e^2}{a^3}\,p = .366\,\frac{\delta_e^2\cdot e^2}{a}\,\frac{p}{(p-1)^2} \tag{69}$$

11. Results of the calculations.

By equations (37), (48), (52), (55), and (69) we can write for the total change in energy:

$$(p-1)\overline{\Delta E} = \left\{1.14 - 0.366\frac{p}{p-1} + 0.0114(p+1)\right\}\delta_e^2 - 7.66\,\frac{p-2}{p-1}\,\delta_e^3$$
$$- \frac{2(p-1)}{p}\left\{\frac{1}{1+\delta_e} - 1 + \delta_e - \delta_e^2 + \delta_e^3\right\} + \frac{0.0583(p-1)}{p}\left\{\frac{1}{(1+\delta_e)^9} - 1 + 9\delta_e - \frac{9\cdot 10}{2}\delta_e^2 + \frac{9\cdot 10\cdot 11}{2\cdot 3}\delta_e^3\right\}$$

Or:

$$p\overline{\Delta E} = 1.942 - 1.475\,\delta_e + \left\{\frac{p}{p-1}\cdot 1.14 - 0.63 - 3.66\left(\frac{p}{p-1}\right)^2 + 0.0114\,\frac{(p+1)p}{p-1}\right\}\delta_e^2$$
$$+ \left\{7.6 - \frac{p(p-2)}{(p-1)^2}\cdot 7.66\right\}\delta_e^3 - \frac{1}{1+\delta_e} + \frac{0.0583}{(1+\delta_e)^9} \qquad (70)$$

Hence

$$\frac{\partial \Delta E}{\partial p} = -\frac{1.942}{p^2} + \frac{1.475\,\delta_e}{p^2} + \left\{-\frac{1.14}{(p-1)^2} + \frac{0.63}{p^2} + 0.366\frac{p+1}{(p-1)^3} - \frac{0.0224}{(p-1)^2}\right\}\delta_e^2 - \left\{\frac{7.6}{p^2} - \frac{p-3}{(p-1)^3}\cdot 7.66\right\}\delta_e^3$$
$$+ \frac{2}{p^2}\frac{1}{1+\delta_e} - \frac{0.0583}{p^2}\frac{1}{(1+\delta_e)^9}$$

Or, to good approximation, for p fairly large:

$$p^2\frac{\partial \Delta E}{\partial p} = 0 = -1.942 + 1.475\,\delta_e + \left\{-1.14 + 0.63 + \frac{p+1}{p-1}\,0.366 - 0.0224\right\}\delta_e^2 - \left\{7.6 - 7.66\frac{p-3}{p-1}\right\}\delta_e^3$$
$$+ \frac{2}{1+\delta_e} - \frac{0.0583}{[1+\delta_e]^9} \qquad (71)$$

so that

$$p = \frac{15.4\,\delta_e^3 - 0.906\,\delta_e^2 + 1.475\,\delta_e - 1.942 + \dfrac{2}{1+\delta_e} - \dfrac{0.0583}{(1+\delta_e)^9}}{0.05\,\delta_e^3 - 0.174\,\delta_e^2 + 1.475\,\delta_e - 1.942 + \dfrac{2}{1+\delta_e} - \dfrac{0.0583}{(1+\delta_e)^9}}$$

For different values of δ_e this gives:

δ_e	=	1	0.9	0.8	0.7	0.6	0
p_p	=	37	34	30	$2\overset{5}{3}$	22	2

By the other minimum condition:

$$p\frac{\partial(\Delta E)}{\partial \delta} = 0 = -1.475 + 2\left\{1.14\frac{p}{p-1} - 0.63 - 0.366\left(\frac{p}{p-1}\right)^2 + 0.0114\,\frac{(p+1)p}{p-1}\right\}\overset{\delta_e}{\downarrow} + 3\left\{7.6 - 7.66\frac{p(p-2)}{(p-1)^2}\right\}\delta_e^2 + \frac{2}{(1+\delta_e)^2} - \frac{0.525}{(1+\delta_e)^{10}}$$

Giving
$$p = \frac{1.475 - 0.288\,\delta_e + 0.18\,\delta_e^2 - \dfrac{2}{(1+\delta_e)^2} + \dfrac{0.525}{(1+\delta_e)^{10}}}{2\times 0.0114\,\delta_e} \qquad (72)$$

For different values of δ_e this gives:

δ_e	=	1	0.9	0.8	0.7	0.6	0.5	0.3	0
p	=	37	39	40	43	$4\overset{3}{2}$	42	41	42

Equations (71) and (72) are therefore seen to have a simultaneous solution at p = 37 and $\delta_e = 1$. The value of the change in energy at this minimum is given by equation (70). It is:

$$\Delta E = \frac{e^2}{a} \frac{0.026}{37} = 5.5 \times 10^{-15} \text{ ergs/ion} \qquad (73)$$

Compare: $$\frac{1}{2} kT = 20.5 \times 10^{-15} \text{ ergs/ion} \qquad (74)$$

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