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HYDROGEN OVERPOTENTIAL ON MERCURY AT LOW CURRENT DENSITIES. II. CONCENTRATED SOLUTIONS OF HYDROCHLORIC ACID

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Part I¹ reported measurements of hydrogen overpotential in acidified solutions of potassium iodide. At low current densities the slope of the polarisation curve plotted in semilogarithmic coordinates was found to be close to 59 mV, the overpotential being independent of the composition of the solution or the structure of the double layer in the region of this slope, whereas at higher potentials, where the slope exceeded 100 mV, the influence of these factors was extremely great. This pattern corresponds closely to the transition from normal slow discharge to the previously predicted² barrierless discharge.

Barrierless discharge is possible only at relatively low cathodic potentials. Therefore the change from ordinary to barrierless discharge can be observed only in solutions in which the overpotential of the former type of discharge is comparatively low. In Part I acidified solutions of a salt of the strongly adsorbed iodide anion were chosen to

provide these conditions. The present paper reports results for concentrated solutions of hydrochloric acid, alone and with additives.

EXPERIMENTAL

The experimental technique has been described in detail in Part I¹. As before, hydrochloric acid was purified by being distilled four times. Stronger solutions were prepared by saturating the four-times distilled acid with gaseous hydrogen chloride, obtained by the action of H_2SO_4 of "chemically pure" quality on twice distilled hydrochloric acid and washed with the four-times distilled acid. Potassium iodide and bromide of "chemically pure" quality were recrystallised twice (the second time from twice distilled water).

In hydrochloric acid, in contrast to KI solutions, the potential was established rapidly at all the current densities studied. The difference between the step-up and step-down curves obtained with the same solution of HCl did not usually exceed 4–5 mV, most of the points coinciding within 2–3 mV. Results of experiments with different portions of solution of the same composition agreed to within 3–5 mV.

For all HCl concentrations our results at current densities above 10^{-7} A cm^{-2} are close to those of Iofa³, although they show a rather smaller slope of the polarisation curve (~100 mV compared with ~110 mV in Ref. 3) and lie 20–40 mV higher. It must be emphasised that later results from the same laboratory^{4,5} also somewhat exceed the earlier data³, and agree with the present results within the limits of experimental error†. All the data for 6 N HCl are compared in Fig. 1.

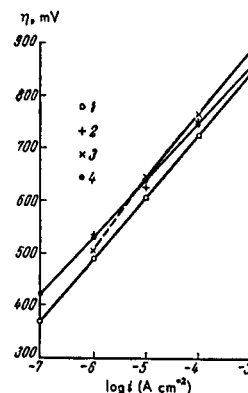


Fig. 1. Polarisation curves in 6 N HCl at 25°C:

1) interpolated data^{3,8}; 2) data from Ref. 4; 3) data from Ref. 5 with concentration and temperature corrections^{3,8}; 4) author's data.

† It may be noted also that, at higher current densities in 5 N HCl, results reported in Ref. 6 (after correction for the conditions of operation of the dropping electrode) are ~30–50 mV above those of Ref. 3, and those in Ref. 7 are 20–30 mV higher.

DISCUSSION

Fig. 2 shows typical polarisation curves obtained in HCl of different concentrations. As in KI solutions, the slope of the polarisation curve is close to 60 mV at low current densities, with good adherence to a semilogarithmic relationship. As has been discussed in detail in Part I,¹ this phenomenon cannot be associated with experimental errors, such as the effect of impurities, concentration polarisation, or spontaneous dissolution of the cathode. An appreciable spontaneous dissolution current could have been expected only in the most concentrated HCl solutions, at current densities close to 10^{-8} A cm⁻² (i.e. considerably below the bend in the polarisation curve). However, even this effect should disappear rapidly, since with a thin layer of solution appreciable accumulation of mercury in the volume ensues quite rapidly, and the diffusion current decreases substantially, as calculation shows.

As with KI solutions, experiments were made on the effect of stirring on the electrode potential in the region with $b = 60$ mV.¹ They confirmed that the change in slope cannot be explained by the effect of impurities, by concentration polarisation, or by spontaneous dissolution of the mercury.

In the previous paper arguments were put forward which, at least for the mercury electrode, refuted the various earlier explanations of the slope of about 60 mV — as due to the shape of the adsorption isotherm¹⁰, the slowness of surface diffusion¹¹, the effect of the zero-charge point¹¹ — the last of which especially requires consideration.

In the present case this explanation is disproved by the fact that the zero-charge points in HCl lie at considerably more negative potentials than the bends in the curves. Thus in 9.8 N, 10.7 N, and 11.7 N HCl the zero-charge points lie at potentials of -0.70, -0.74, and -0.78 V relative to a hydrogen electrode in the same solution¹², whereas the bends on the polarisation curves in these solutions occur at -0.31, -0.34, and -0.35 V, i.e. in a completely different range.

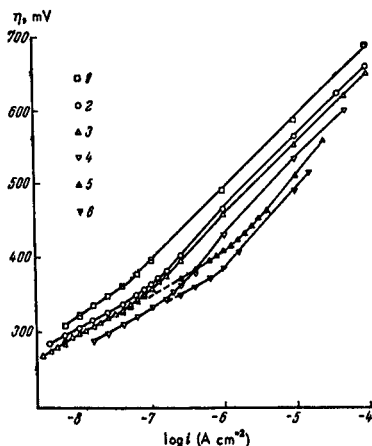


Fig. 2. Typical polarisation curves in HCl solutions differing in composition:

- 1) 8.85 N; 2) 10.5 N; 3) 11.3 N; 4) 12.5 N;
- 5) 11.3 N saturated with KBr; 6) 12.5 N saturated with KBr.

In acid potassium iodide solutions the value of $b \approx 60$ mV is well explained by a transition to the barrierless discharge of H_3O^+ ions¹. In conformity with theory² the overpotential is then independent of the composition of the solution. In concentrated HCl, in contrast to this, the dependence of overpotential on acid concentration is almost the same whether b is ~ 60 or ~ 100 mV. At first glance this type of variation corresponds to the process of non-activated electrochemical desorption examined earlier¹³, which would have been possible at low potentials if barrierless discharge had not occurred. More detailed analysis shows, however, that actually agreement is not present here. Thus the addition of KBr, while greatly depressing the overpotential in the range $b \approx 100$ mV, has hardly any effect on it at low current densities. Similarly, the effect of added KI is considerably stronger above than below the bend in the curve. Such behaviour is not consistent with slow non-activated desorption, since an almost equal decrease in overpotential must then have been expected for the two sections of the polarisation curve.

Thus neither of the mechanisms considered above — barrierless discharge of H_3O^+ and non-activated desorption — can completely explain the situation observed experimentally in concentrated solutions of HCl, without allowance for some additional factors which depress the overpotential. I suggest that, in discussion of the evolution of hydrogen from concentrated solutions of strong acids, account must be taken of the possible discharge of, together with H_3O^+ ions, undissociated molecules of the acid, which are considerably more active proton-donors than H_3O^+ , and in very strong solutions are already present in appreciable concentrations.

The hypothesis that molecules of the acid (or the corresponding associated ion-pairs) take part in the cathodic process was first put forward by Durdin¹⁴. This view was later held by de Bethune and Kimball¹⁵, but their experimental results were extremely unreliable, and could hardly serve as a basis for this hypothesis. Frumkin and Iofa^{3,16} attribute several features of the adsorption behaviour of halide anions to the formation of undissociated molecules of the acids. Interesting arguments for the existence of such molecules in the double layer in concentrated solutions have been found by Durdin and Tsventarnyi¹⁷, who have observed a decrease in the capacitance of the double layer in the region of strong adsorption of the acid.

Quantitative examination of the problem, in a similar manner to that used for H_3O^+ ions^{2,13}, yields the following expressions for normal and barrierless discharge of HX molecules

$$i_{HX} = \frac{kT\epsilon}{h} \kappa(1-\theta) \frac{1}{\gamma^{**}} 10^{15} 56^{-4} a_{HX}^0 p_{H_2}^{1/2} a_{X^-}^{-\alpha} \exp\left\{-\frac{1}{RT} \times \right. \\ \left. \times \left[\Delta H_{\infty}^{**} + \alpha \Delta H_{a-H} + \alpha \Delta G_{a-X}^{00} + \beta \Delta G_{a-HX}^{00} + \frac{1}{2} \alpha T S_{H_2} \right] \right\} \exp \frac{\alpha(\eta + \psi_1)F}{RT} \quad (1)$$

$$i_{HX} = \frac{kT\epsilon}{h} \kappa(1-\theta) \frac{1}{\gamma^{**}} 10^{15} 56^{-4} p_{H_2}^{1/2} a_{X^-}^{-\alpha} \exp\left\{-\frac{1}{RT} \left[\Delta H_{a-H} + \Delta G_{a-X}^{00} + \right. \right. \\ \left. \left. + \frac{1}{2} T S_{H_2}^{00} \right] \right\} \exp \frac{(\eta + \psi_1)F}{RT} \quad (2)$$

in which the notation is similar to that employed previously.

One peculiarity of the barrierless discharge of molecules compared with that of H_3O^+ ions must be noted. In the latter case, as mentioned above, the overpotential should not necessarily depend on the acid concentration (at

least in dilute solutions) or the ψ_1 potential. In the discharge of HX the situation is different. Since the HX species is neutral, its surface concentration will not depend on the ψ_1 potential (at least to a first approximation), and thus there is nothing to balance the effect of ψ_1 on the potential drop in the dense part of the double layer, and hence on the rate of discharge. On the other hand, although the activity of the proton source HX does not occur directly in Eqn. (2) (for the same reasons as apply to the activity of H_3O^+), the rate of this process is very greatly dependent on the acid concentration, since the activity of the corresponding base (the X^- ions) increases rapidly with rise in the acid concentration. In contrast to the discharge of H_3O^+ ions, therefore, the barrierless discharge of HX molecules may depend substantially on the composition of the electrolyte.

Let us try to estimate the possible role of the discharge of acid molecules compared to that of H_3O^+ . From Eqns. (1) and (2) the corresponding equations for the discharge of H_3O^+ it follows that

$$\frac{i_{\text{HX}}}{i_{\text{H}_3\text{O}^+}} = \frac{\gamma_{\text{H}_3\text{O}^+}^*}{\gamma_{\text{HX}}^*} K_d^{\frac{1}{2}} \frac{a_{\text{X}^-}}{a_{\text{H}_3\text{O}^+}} 56^{-\alpha} \exp \left\{ -\frac{1}{RT} [(\Delta H_{\infty}^{\text{H}_3\text{O}^+}(\text{HX}) - \Delta H_{\infty}^{\text{H}_3\text{O}^+}(\text{H}_3\text{O}^+)) + \right. \\ \left. + \alpha (\Delta H_{\text{aH}}(\text{HX}) - \Delta H_{\text{aH}}(\text{H}_3\text{O}^+)) + \alpha (\Delta G_{\text{aX}^-}^{\text{H}_3\text{O}^+} - \Delta G_{\text{aH}_3\text{O}^+}^{\text{H}_3\text{O}^+}) + \right. \\ \left. + \beta (\Delta G_{\text{aHX}}^{\text{H}_3\text{O}^+} - \Delta G_{\text{aH}_3\text{O}^+}^{\text{H}_3\text{O}^+})] \right\} \exp \frac{F}{RT} (\alpha \psi_{\text{HX}} + \beta \psi_{\text{H}_3\text{O}^+}), \quad (3)$$

$$\frac{i_{\text{HX}}^{\#}}{i_{\text{H}_3\text{O}^+}^{\#}} = \frac{\gamma_{\text{H}_3\text{O}^+}^*}{\gamma_{\text{HX}}^*} \frac{a_{\text{X}^-}}{56 a_{\text{H}_3\text{O}^+}} \exp \left\{ -\frac{1}{RT} [(\Delta H_{\text{aH}}(\text{HX}) - \Delta H_{\text{aH}}(\text{H}_3\text{O}^+)) + \right. \\ \left. + (\Delta G_{\text{aX}^-}^{\text{H}_3\text{O}^+} - \Delta G_{\text{aH}_3\text{O}^+}^{\text{H}_3\text{O}^+})] \right\} \exp \frac{\psi_{\text{HX}} F}{RT}. \quad (4)$$

K_d being the dissociation constant of HX†.

The heat content of adsorbed hydrogen obtained by the discharge of HCl is probably rather higher than in the discharge of H_3O^+ , for in the first case the polar M-H bond is repelled from Cl^- ions, not from a neutral water molecule. Assessing this difference as 1–2 kcal, we obtain a factor of the order of 10^{-1} in the expression for $i_{\text{HCl}}^{\#}/i_{\text{H}_3\text{O}^+}^{\#}$.

The value of $\Delta G_{\text{aCl}^-}^{\text{H}_3\text{O}^+}$ has been estimated from the equation

$$\ln \frac{a_{\text{X}^-}(\text{ads})}{a_{\text{X}^-}(\text{bulk})} = -\frac{\Delta G_{\text{aX}^-}^{\text{H}_3\text{O}^+} - \psi_1 F}{RT}$$

the activities being taken as equal to the mole fractions (data on specific adsorption from Refs. 18 and 19), and the potential of the outer ionic layer ψ^0 (from Ref. 19) being used as ψ_1 ; these two assumptions introduce errors which make the value of the adsorption energy rather too high. The value of $\Delta G_{\text{aCl}^-}^{\text{H}_3\text{O}^+}$ calculated in this way diminishes appreciably (in absolute magnitude) as the zero-charge point is approached, but it varies relatively little, between -0.11 and -0.15 eV (per molecule), in the region 0.2–0.4 V more positive than this point. The surface tension of water yields an estimate of $\Delta G_{\text{aH}_2\text{O}}^{\text{H}_3\text{O}^+} \approx 0.46$ eV mol $^{-1}$.

The activity of water was taken from Ref. 20, and a_{Cl^-} was taken as equal to a_{HCl} .²¹

† Analogues of Eqns. (3) and (4) can be obtained by using the Brønsted relation. It must then be remembered that the dissociation constant of the acid in the adsorbed film is not strictly the same as its dissociation constant in bulk, because of the difference in adsorption energy between molecules and ions. Furthermore, application of the Brønsted relation presupposes that the potential curves are of the same form, i.e. the same value of $\Delta H_{\text{H}_3\text{O}^+}^{\#}$ and the same proton-accepting partner for the two acids, i.e. the same ΔH_{aH^+} .

An estimate of ψ_1 ,_{HCl} was obtained on the assumption that the potential of the inner part of the double layer ψ^i constitutes approximately 60% of the shift in the zero-charge point compared with a solution containing no specifically adsorbed anions. However, it would hardly have been correct to use this quantity as the ψ_1 potential, i.e. the potential at the site of the activated complex. It can rather be expected that the ψ_1 potential will have a value intermediate between ψ^i and ψ^0 . For the discharge of H_3O^+ in KI solution, Frumkin has made an estimate of $\psi_1 = -0.124$ V, while ψ^i in a solution of nearly the same composition is -0.188 V.¹⁶ As a rough estimate I have assumed the same ratio between these quantities, i.e. $\psi_1 \approx \frac{2}{3} \psi^i$. §

The above estimates of the different terms in Eqn. (4) have yielded calculated values of -0.04, 0.41, 0.98, and 1.49 for log ($i_{\text{HCl}}^{\#}/i_{\text{H}_3\text{O}^+}^{\#}$) in 3 N, 7 N, 10 N, and 12.5 N HCl. Thus rough calculation shows that barrierless discharge of undissociated acid molecules may be expected to play an appreciable part, and even predominate, in concentrated solutions of acids. This condition inevitably involves a decrease in overpotential with increase in acid concentration.

It is extremely difficult to give even an approximate quantitative estimate of the relative extent to which HX participates in the region of normal discharge. From a comparison of Eqns. (3) and (4) it can be concluded, however, that the ratio $i_{\text{HX}}/i_{\text{H}_3\text{O}^+}$ is probably appreciably smaller than $i_{\text{HX}}^{\#}/i_{\text{H}_3\text{O}^+}^{\#}$.

Hence a qualitative understanding is obtained of why the decrease in overpotential is practically the same in the two ranges: with $b \approx 60$ mV, the whole effect is due to the increase in the HCl discharge current, while at higher current densities two effects are superimposed — that of the shift in ψ_1 potential on the discharge of H_3O^+ and the intensification of the discharge of HCl.

Addition of a salt of an adsorbable anion, e.g. KBr, should increase the overpotential of the barrierless discharge of HCl, but at the same time will provide a new source of protons, HBr molecules. Appropriate estimates show that these two effects may practically balance one another, whereas in the region of normal discharge the

§ Frumkin has remarked^{3,16} that in concentrated HBr the decrease in overpotential is 50–65% of the shift in the zero-charge point, which compares with the analogous ratio between $\Delta \psi_{\text{zc}}$ and ψ^i . It must be remembered, however, that part of the decrease in overpotential is probably due to the discharge of HBr molecules, so that $\Delta \eta$, actually caused by the ψ_1 effect, is less than 50–60% of $\Delta \psi_{\text{zc}}$. This is consistent with the hypothesis that the ψ_1 potential, while being close to ψ^i , is nevertheless smaller than the latter.

¶ The preexponential factors are almost the same in the two cases (K_d being around 30^{22}), while the exponent is probably smaller in the first case. This follows from the following probable assessments

$$\Delta G_{\text{aHX}}^{\text{H}_3\text{O}^+} > \Delta G_{\text{aX}^-}^{\text{H}_3\text{O}^+},$$

$$\Delta G_{\text{aH}_3\text{O}^+}^{\text{H}_3\text{O}^+} > \Delta G_{\text{aH}_3\text{O}^+}^{\text{H}_3\text{O}^+} \times (\Delta H_{\infty}^{\text{H}_3\text{O}^+}(\text{HX}) - \Delta H_{\infty}^{\text{H}_3\text{O}^+}(\text{H}_3\text{O}^+)) > \frac{1}{2} (\Delta H_{\text{aH}}(\text{HX}) - \Delta H_{\text{aH}}(\text{H}_3\text{O}^+)),$$

where

$$\Delta H_{\infty}^{\text{H}_3\text{O}^+}(\text{HX}) > \Delta H_{\infty}^{\text{H}_3\text{O}^+}(\text{H}_3\text{O}^+)$$

because the activated complex is more distant from the cathode, and for the same reason

$$\psi_{\text{H}_3\text{O}^+} < \psi_{\text{HX}}.$$

principal part is played by the decrease in overpotential of H_3O^+ discharge due to the shift in ψ_1 potential.

All the above calculations, of course, are tentative in character, and cannot be regarded as proof of the correctness of the hypothesis put forward above. However, they show that the assumption of the barrierless discharge of hydrogen halide acid molecules provides a qualitative explanation of the observed pattern, without, it appears, recourse to any contradictory postulates.

A direct indication of the barrierless discharge of acid molecules is given by data on the effect on overpotential of the addition of a tetrabutylammonium salt to strongly acid solutions of potassium iodide.

The invariability of overpotential with composition previously found in acidified KI solutions can be observed, of course, only to the extent to which the discharge of HCl or HI molecules does not become effective. Thus in $0.8\text{ N KI} + 6.0\text{ N HCl}$, $2.5\text{ N KI} + 2.6\text{ N HCl}$, and some other solutions the overpotential is substantially lower. The mean ionic molarity $c_{\pm\text{HI}} = \sqrt{c_{\text{H}^+}c_{\text{I}^-}}$ can be taken as a very rough measure of the probability that undissociated HI molecules are present in the solution. Fig.3 shows the overpotential at $i = 10^{-6}\text{ A cm}^{-2}$ as a function of $c_{\pm\text{HI}}$. It is seen that the overpotential falls appreciably beginning from $c_{\pm\text{HI}} \approx 2.1$, and this can be attributed to the discharge of HI molecules.

Fig. 4 includes, together with previously published data on weakly acid KI solutions¹, polarisation curves in strongly acid KI with and without the addition of tetrabutylammonium. The adsorption of $\text{N}(\text{C}_4\text{H}_9)_4^+$ intensifies the effect of I^- ,²³ and therefore a decrease in overpotential could have been expected in the region of high b (acceleration of the discharge of H_3O^+ ions) and an increase at $b \approx 60\text{ mV}$ (retardation of the discharge of HI and absence of any effect on the barrierless discharge of H_3O^+). This is precisely the pattern observed experimentally†.

Barrierless discharge, like any discharge process, should in general be affected also by the structure of the double layer. The absence of this influence in the discharge of H_3O^+ ions is due, as explained earlier^{1,2}, to the exact balancing of the two opposing effects of these factors on the surface concentration of the ions and on the potential difference which accelerates the discharge. With uncharged species — the acid molecules — such compensation is lacking, and therefore a substantial dependence of overpotential on solution composition is found. This fact is of fundamental importance, since it shows that we are in fact

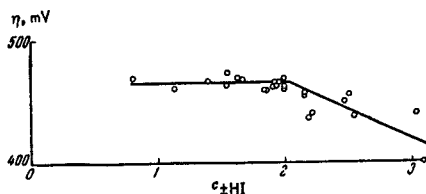


Fig. 3. Dependence of hydrogen overpotential at 10^{-6} A cm^{-2} on mean ionic molarity of HI .

† It may be noted that the difference in sign between the effects of tetrabutylammonium in the regions of high and of low slope cannot be explained by non-activated electrochemical desorption.

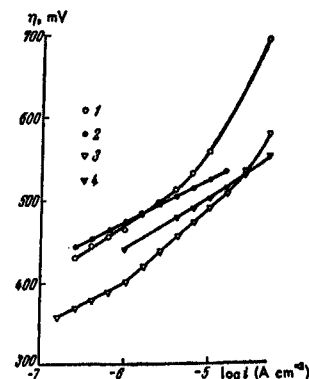


Fig. 4. Effect of tetrabutylammonium on hydrogen overpotential in KI solutions differing in acidity: 1) $6.0\text{ N KI} + 0.4\text{ N HCl}$; 2) as (1) + 10^{-3} N tetrabutylammonium; 3) $2.2\text{ N KI} + 4\text{ N HCl}$; 4) as (3) + 10^{-3} N tetrabutylammonium.

dealing with a discharge process, and not with some reaction such as recombination, in which components of the solution are not involved.

SUMMARY

Measurements have been made of hydrogen overpotential in concentrated solutions of HCl up to current densities of about 10^{-8} A cm^{-2} and in strongly acid KI solutions up to about 10^{-7} A cm^{-2} . At low current densities in all the solutions investigated, a linear relation is found between overpotential and logarithm of current density, with a coefficient $b \approx 60\text{ mV}$. At higher current densities $b \gtrsim 100\text{ mV}$. In strongly acid solutions the overpotential in the range having $b \approx 60\text{ mV}$ depends substantially on the acid concentration and on the addition of specifically adsorbed ions.

The regularities which have been found are well explained by the barrierless discharge of undissociated molecules (or of the corresponding ion-pairs).

NOTED ADDED IN PROOF

In Part I¹, owing to the author's mistake, the KI concentration of 6.0 N was always printed as 6.8 N .

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ENTROPY OF SYSTEMS CONTAINING IONS

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Any system of particles is characterised by a definite statistical distribution, resulting in the formation of a characteristic statistical lattice. These lattices may be either atomic, molecular, or ionic, or it may be mixed (atomic-ionic, molecular-ionic, etc.). The distribution of atoms and molecules in a statistical lattice is determined by the methods of statistical thermodynamics, and can be characterised by the entropy of the particles constituting the system. The distribution of ions in a statistical lattice has several peculiarities, and requires special consideration. The simplest system containing ions is an ideal ionic gas. For this reason the present paper examines mainly the peculiarities of the distribution of ions in an ideal ionic gas, on the basis of its entropy characteristics.

Since on the macroscopic scale an ionic gas must be electrically neutral, it consists of an inseparable aggregate of oppositely charged particles. As a result, the additional condition is superimposed on the canonical distribution of ions that a given macroscopic volume must contain equal numbers of charges of opposite sign.

The peculiarities of the statistical distribution of ions can be allowed for¹ either by introducing an additional

term into the equations used for the calculations or by choosing a new standard state to provide the same datum level for the thermodynamic functions of both neutral and charged species.

The standard state of a neutral gas at any temperature is usually taken as the hypothetical state in which its fugacity is 1 atm. For ideal gases this state is identical with the state of the gas at a pressure of 1 atm.

I have taken as the standard state of an ideal ionic gas at any temperature its hypothetical state, at a pressure of 1 atm, in which the statistical distribution of the ions is the same as that of neutral particles under the same conditions¹. This choice of standard state for an ionic gas, while achieving a single level for reckoning the entropies of neutral and charged species, nevertheless does not take into account the real statistical distribution of the ions. For this reason we must choose as standard state of an ideal ionic gas at any temperature its hypothetical state at a pressure of 1 atm in which the statistical distribution of the ions corresponds to the actual distribution under the same conditions.

We can obtain the change in entropy of the ionic gas on passing from one standard state to the other from the well-known thermodynamic formula for the change in entropy accompanying the mixing of two different ideal gases at the same temperature and pressure

$$\Delta S = -n_1 R \ln N_1 - n_2 R \ln N_2 = n_1 \Delta S_1 + n_2 \Delta S_2, \quad (1)$$

where $\Delta S_1 = -R \ln N_1$ and $\Delta S_2 = -R \ln N_2$, with n_1 and n_2 being the numbers of moles of the two different miscible gases at the same temperature and pressure, and N_1 and N_2 the mole fractions of these gases in the mixture. The mixing of two different gases results in the formation of a mixed atomic or molecular statistical lattice, in which the distribution of particles differs from their distribution in the individual gas. A quantitative measure of this difference is provided by the value of ΔS .

An ionic gas exists as an inseparable combination of oppositely charged species. For this reason a feature of the distribution of ions in the gaseous state is the formation of a peculiar ionic statistical lattice governed by an alternation of oppositely charged particles and existing as a time average².

From what has been said above, the change in entropy accompanying the mixing of ideal ionic gases (a cationic gas and an anionic gas) is given by Eqn. (1). It is interesting to note that the entropy change accompanying formation of a mixed ionic statistical lattice from the ionic statistical lattices of the ideal cationic and anionic gases is always positive, since N_1 and N_2 are less than or equal to unity.

The relationship between the entropies of ideal ionic gases having the real distribution of charged particles — $S_{M(gas)}^{z_C}$ and $S_{X(gas)}^{z_A}$ — having the distribution characteristic of a neutral gas — $S_{M(gas)}^{z_C}$ and $S_{X(gas)}^{z_A}$ — given by the equation

$$n_C S_{M(gas)}^{z_C} + n_A S_{X(gas)}^{z_A} = n_C S_{M(gas)}^{z_C} + n_A S_{X(gas)}^{z_A} + \Delta S, \quad (2)$$

where n_C and n_A are the numbers of moles of the cationic and anionic gases, and z_C and z_A are the charges on the cation and the anion. Substitution of Eqn. (2) in (1) followed by rearrangement yields

$$n_C S_{M(gas)}^{z_C} + n_A S_{X(gas)}^{z_A} = n_C (S_{M(gas)}^{z_C} + \Delta S_1) + n_A (S_{X(gas)}^{z_A} + \Delta S_2). \quad (3)$$