

theory has been criticised also in the recent paper by Fisher and Kopeliovich³, who remark that the form $g_3 = 1 + (\gamma/V^2)$ is inconsistent with the condition of weakening of the statistical correlation.

The integral equation (11), while less compact, has the advantage over the Richardson equation that, when the solution is expanded in powers of the density, the terms of first and second degree are identical with the exact expressions, while the second, third, and fourth virial coefficients appear in the virial equation of state. A further improvement is achieved by taking into account terms of the order ρ^3 in Eqn. (10). The corresponding integral equation is not written out because of lack of space.

Recently direct summation methods have been used to find a closed integral equation for the binary distribution function⁵⁻⁹. In the hypercatenary approximation, when the elementary diagrams⁵, including also diagram (d), are neglected, the following equation⁸ is obtained:

$$\ln F_2^N(12) = -\beta u(12) + \rho \int \Delta F_2^N(13) \Delta F_2^N(23) d3 - \rho \int [\ln F_2^N(13) - \beta u(13)] \Delta F_2^N(23) d3. \quad (12)$$

If the potential of the mean force $kT \ln F_2^N$ is replaced by the conjugate potential u , Eqn. (12) passes into Richardson's equation. Our Eqn. (11) is in a sense more exact than Eqn. (12), since it passes into the latter if the simplest elementary diagram (d) is neglected. This can be shown by applying to Eqn. (12) an iteration procedure, and substituting the conjugate potential for the potential of the mean force in the equation obtained after the first step. Recently Verlet⁹ has obtained an integral equation differing from Eqn. (12) precisely by the term represented by diagram (d).

It is readily seen that Verlet's iteration method yields results identical with those of the variation theory to the simplest (3, 3)-approximation. However, the version of the variation theory described here has several advantages, in that it is possible, with an appropriate choice of a trial binary distribution function, to compute directly the integrals in the free energy. Furthermore, the formal analogy between the problem of calculating integral (8) and that of calculating the binary distribution function in Gibbs's statistical mechanics enables recently developed direct methods of summation to be used to improve further the (3, 3)-approximation.

APPENDIX

Proof of Theorem C

When $n = 2$ the statement of the theorem is self-evident¹¹. For any n , strong conditions of normalisation require that the integral

$$\int \dots \int_V \Delta F_n^N(1 \dots n) \frac{d1 \dots dn}{V^n} \quad (A)$$

should vanish at all values of V . Let us show that a set of constants $B_2, \dots, B_{n-1}$ in the expression $\Delta \varphi_n^N = \lim_{V \rightarrow \infty} \Delta \varphi_n^N + B_n/V^{n-1} + \dots$ can be chosen such that all contributions of the order of $V^{-1}, \dots, V^{-(n-2)}$ in (A) vanish. Actually, if strong conditions of physical compatibility are satisfied, and F_n^N satisfies a strong condition of normalisation, then all functions F_m^N ($m < n$) also are subject to strong normalisation, which consequently imposes no additional restrictions on the coefficients $B_2, \dots, B_{n-1}$. The

possibility of the required choice is now obvious, since we have $n - 2$ non-homogeneous algebraic equations from which to determine $n - 2$ coefficients.

Among terms of the order of $V^{-(n-1)}$ in (A) is the integral $\int \dots \int_V \Delta \varphi_n^N d1 \dots dn / V^n$, which vanishes only if $\Delta \varphi_n^N$ contains a component of the order of $V^{-(n-1)}$. Otherwise, additional functional relations would have to be introduced between the functions $\lim_{V \rightarrow \infty} \Delta \varphi_n^N$. Hence the function $\Delta \varphi_n^N$ must contain terms of the order of $V^{-(n-1)}$, and no components of the order of V^{-t} with $t < n - 1$.

SUMMARY

New possibilities for a theory of the liquid state are offered by the variation theory of molecular distribution functions. In contrast to Richardson's earlier work, attention is paid mainly to analysing the restrictions which must be imposed on the distribution functions in order to satisfy the general relations of probability theory. A criterion is suggested by means of which unobserved contributions to the free energy can be segregated. An integral equation is formulated for the binary distribution function which is comparable in exactness with results of direct methods of summing statistical integrals.

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RADIOCHEMICAL AND ELECTROCHEMICAL STUDY OF ELECTRODE PROCESSES ON AMALGAMS. III

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Electrode processes on thallium and indium amalgams have been investigated by a method previously described¹. Exchange currents on thallium amalgams were measured

in 0.00014–0.06 M solutions of TlClO_4 with 0.002–5 M amalgams, at a constant ionic strength of 3 M maintained by NaClO_4 , and also on 0.1–0.4 M amalgams at an ionic strength of 0.1 M. Experiments with different amalgam concentrations were done in a 0.03 M solution of TlClO_4 .

The effect of TlClO_4 concentration on the rate of exchange and on the limiting cathodic current is shown in Fig. 1. The exchange rates, measured radiochemically, and the limiting currents, deduced from electrochemical measurements, have very similar values and lie on parallel straight lines of approximately unit slope (0.96). It follows that under these conditions the exchange rate is determined by the rate of diffusion of thallium ions in solution². The effect of amalgam concentration on the exchange rate in a solution of ionic strength 3 M (Fig. 2) and 0.1 M is substantially the same: at low amalgam concentrations the exchange rate and the anodic limiting current lines (lines 1 and 2, respectively) are parallel, close together, and their slope is almost unity. For amalgam concentrations higher than 0.02 M, when $i_a^c > i_d^c$ and diffusion of radioactive thallium

species in solution begins to limit the exchange process, the rate of exchange should be substantially independent of the amalgam concentration. However, Fig. 2 shows a slight but significant increase in exchange rate at high amalgam concentrations for which there is no satisfactory explanation†.

From a comparison of the anodic and the cathodic limiting currents with the corresponding exchange rates, we conclude that the thallium amalgam cannot be studied (owing to its large exchange current) at concentrations such that the process is limited by the rate of discharge and ionisation, as is the case with zinc amalgams¹. Mixed control is observed only over a small section of the curve (between 0.02 and 0.04 M amalgam concentrations in Fig. 2), and diffusion in the amalgam and in solution contributes very significantly to rate-limitation in this region. The measured

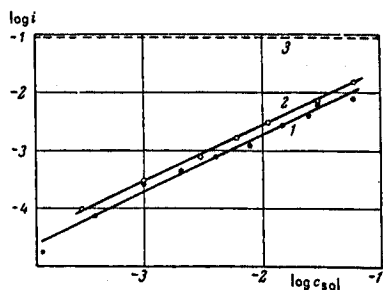


Fig. 1. Effect of TlClO_4 concentration (at $c_a = 0.2$ M and $\mu = 3$ M) on: 1) exchange rate; 2) cathodic limiting current; 3) anodic limiting current.

† Miller³ also reported a very slight increase in exchange rate at the highest thallium amalgam concentrations (0.1–6 at.%) in a 0.1 M Tl_2SO_4 solution. At these relative concentrations of amalgam and solution the rate of exchange should be determined by diffusion in the solution, and should be independent of the amalgam concentration.

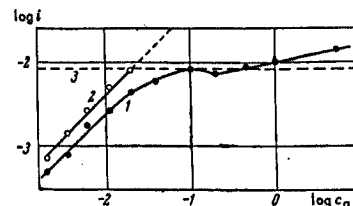


Fig. 2. Effect of thallium amalgam concentration (at $c_{\text{sol}} = 0.03$ M and $\mu = 3$ M) on: 1) exchange rate; 2) anodic limiting current; 3) cathodic limiting current.

rates of exchange are too close to the limiting currents for reliable calculation of the exchange current in this region†. We have tried an approximate evaluation of the transfer coefficients for thallium amalgams by analysing polarisation curves as in Eqn. (16) of Ref. 2, using experimentally observed limiting currents and the expression $\alpha + \beta = 1$. The calculated polarisation curve is fitted to the experimental points by selecting the most suitable values of the exchange current and of the transfer coefficients. The values $\alpha = 0.4$ and $\beta = 0.6$, obtained by this procedure for a large number of polarisation curves, are entirely reasonable and in good agreement with Randles' value⁵ $\alpha = 0.5$.

The temperature variation of the rate of exchange (Fig. 3) corresponds to an activation energy of 2.1 kcal mole⁻¹, calculated from the slope of the plots§.

The exchange currents on zinc and thallium amalgams are so large, especially the latter, that we were unable to study the rate of the true anodic process as a function of potential: concentration polarisation effects were significant even at small departures from the equilibrium potential. The method was therefore applied to the study of electrode processes on a low-exchange-current metal (indium amalgam) under clean conditions. The true rate of the anodic process (i_a) on indium amalgam was measured as a function of electrode potential at amalgam concentrations between 0.002 and 0.9 M in 0.0004–0.03 M solutions of $\text{In}(\text{ClO}_4)_3$, in the presence of 0.01 M HClO_4 and of an excess of NaClO_4 to keep the ionic strength at 3 M (20°).

Fig. 4 gives the variation of $\log i_a$ with potential, and the conventional polarisation curves, plotted in the same experiment from the measured current. Even at strong cathodic polarisations of the amalgam ionisation of the indium proceeds at an appreciable rate, the logarithm of i_a varying linearly with potential. When the departure from the equilibrium potential is sufficiently large and positive, the

‡ The point for a 0.1 M amalgam concentration on curve 1 of Fig. 2 is definitely out of line. This effect is very small because the rate of exchange and the limiting cathodic current have very similar values, but it cannot be dismissed as experimental error, particularly since a kink in the exchange rate curve at this amalgam concentration can also be observed in a solution of ionic strength 0.1 M. Since the effect occurs at potentials close to the zero-charge potential of the thallium amalgam⁴, it would appear to be related to amalgam surface charge-transfer effects.

§ A similar activation energy (2 kcal mole⁻¹) has been reported⁶ for the $\text{Hg}-\text{Hg}_2^{2+}$ system, where the exchange current is very high. It probably refers to the discharge-ionisation stage.

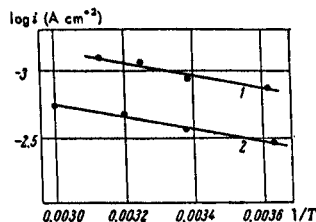


Fig. 3. Temperature variation of exchange rate on thallium amalgam for $c_{\text{sol}} = 0.03$ M and different amalgam concentrations (c_a , M): 1) 0.2; 2) 0.02.

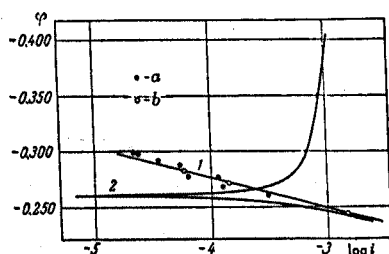


Fig. 4. True anodic curve (1) and polarisation curves (2) for $c_a = 0.1$ M and $c_{\text{sol}} = 0.03$ M: a) exchange current; b) true rate of the anodic process, i_a .

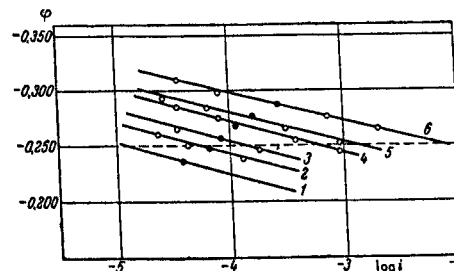


Fig. 5. True anodic curves for different indium amalgam concentrations (c_a , M): 1) 0.002; 2) 0.0075; 3) 0.025; 4) 0.1; 5) 0.3; 6) 0.9. $c_{\text{sol}} = 0.01$ M $\text{In}(\text{ClO}_4)_3$.

whence we may conclude that the rate of the electrochemical process is determined by the rate of the discharge-ionisation stage†. The plots (Fig. 5) of $\log i_a$ against potential for different amalgam concentrations c_a are displaced towards more negative potentials on increasing c_a , but retain a constant slope‡. The dotted line at $\varphi = -0.250$ V intersects the anodic curves at the i_a values (corresponding to different c_a and $\varphi = \text{const}$) plotted in Fig. 6. The logarithmic relationship is linear with unit slope, showing that the rate of the anodic process is directly proportional to the amalgam concentration. The transfer coefficient α was evaluated from the variation of exchange current with equilibrium potential at different values of c_a and constant $\text{In}(\text{ClO}_4)_3$ concentration. In Fig. 7 are plotted the true rate of the cathodic process (from exchange currents), the true rate of the anodic process, and the corresponding polarisation curves for the same solution and $c_a = 0.3$ M. The function $(\varphi_{\text{eq}} - \log i_0)_{c_{\text{sol}}}$ is linear with a slope of 0.065 V, whence $\alpha = 2.3RT/F(\partial \varphi_{\text{eq}}/\partial \log i_0)_{c_{\text{sol}}} = 0.91 \pm 0.02$.

The variation with c_{sol} of the true rate of the cathodic process i_c can be evaluated by drawing cathodic curves of φ versus $\log i_c$, with a slope of 0.065 V, through points corresponding to the exchange currents for different c_{sol} and constant c_a (Fig. 4). The variation of $\log i_c$ with $\log c_{\text{sol}}$ at $\varphi = \text{const}$ was found to be linear, with unit slope. Hence the

points of the radiochemical experiment coincide with those of the anodic polarisation curve¶. The slope of the straight line is $b_a = 0.0265$ V, and corresponds to a transfer coefficient $\beta = 2.3RT/b_a F = 2.20 \pm 0.07$. The figure also shows the exchange currents i_0 at the equilibrium potentials for different $\text{In}(\text{ClO}_4)_3$ concentrations between 0.0004 M and 0.03 M: these lie on the linear anodic plot, indicating that the rate of the process is independent of the concentration of In^{3+} ions. True anodic curves, whether plotted by the radiochemical method or constructed from the exchange currents at different solution concentrations, have identical slopes,

¶ Since the i_a values were computed from radiochemical data¹ on the assumption that the anodic process gives rise exclusively to trivalent indium ions ($n = 3$), it follows that the current efficiency of the anodic dissolution of indium is close to 100%. Thus the end-product of the anodic process must consist of In^{3+} ions, since the current efficiency of the anodic process would exceed 100% if lower-valency indium ions were oxidised in solution rather than at the electrode to a significant extent.

† The equations for the true rate of an anodic process, in conjunction with the expression for the variation of exchange current with equilibrium potential [Eqn. (9) of Ref. 2] show that these curves must coincide if the amalgam concentration is the same. Hence the $\varphi - \log i_a$ and the $(\varphi_{\text{eq}} - \log i_0)_{c_a}$ curves should have identical slopes. Of course, the $(\varphi - \log i_c)$ and the $(\varphi_{\text{eq}} - \log i_0)_{c_{\text{sol}}}$ curves must also coincide. It follows that transfer coefficients can be evaluated, either from the slope of the true rates of the anodic and the cathodic process, or from the slope of the $(\varphi_{\text{eq}} - \log i_0)$ curves, using the relations

$$(\partial \varphi_{\text{eq}} / \partial \log i_0)_{c_a} = \frac{2.3 RT}{\beta F} \quad \text{and} \quad (\partial \varphi_{\text{eq}} / \partial \log i_0)_{c_{\text{sol}}} = -\frac{2.3 RT}{\alpha F},$$

which readily follow from Eqn. (9) of Ref. 2.

‡ At the lowest amalgam concentration only the exchange current was measured, and an anodic curve of slope $b_a = 0.0265$ V was drawn through this point.

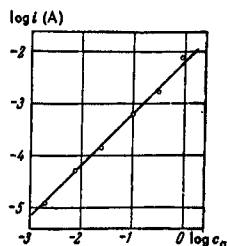


Fig. 6. Effect of indium amalgam concentration on the rate of the anodic process at constant potential ($\varphi = -250$ mV).

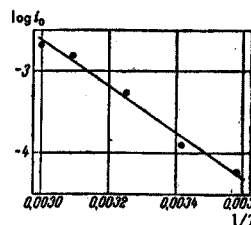


Fig. 8. Temperature variation of the exchange current at $c_{\text{sol}} = 0.01$ M $\text{In}(\text{ClO}_4)_3$ and $c_a = 0.01$ M.

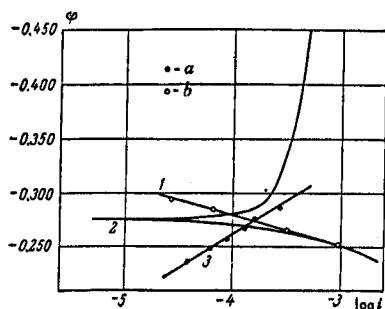


Fig. 7. True anodic curve (1) and polarisation curves (2) for $c_a = 0.3$ M and $c_{\text{sol}} = 0.01$ M; true cathodic curve (3) plotted from exchange currents at different indium amalgam concentrations (0.002–0.9 M): a) exchange current; b) true rate of the anodic process.

true rate of the cathodic process is proportional to the concentration of In^{3+} ions. As in the case of zinc, the sum of the transfer coefficients for indium amalgams is approximately equal to the total number of electrons involved in the electrode process ($\alpha + \beta = 3.11$). Using Eqn. (12) of Ref. 2, the variation of exchange current with amalgam and solution concentration may be represented by the expression

$$i_0 = {}^0i_0 [\text{In}]^{0.30} [\text{In}^{3+}]^{0.78}, \quad (1)$$

where ${}^0i_0 = 0.0067$ A cm^{-2} .

The temperature-dependence of the exchange current between 6° and 60° (Fig. 8) leads to an activation energy of 12.8 kcal mole^{-1} .

Unlike the corresponding anodic curves, the curve giving the true rate of the cathodic process and the conventional cathodic polarisation curve (Fig. 7) diverge rapidly when the electrode potential is displaced from its equilibrium value: the slope of the cathodic polarisation curve is much

§ This value, obtained from improved data, differs somewhat from our previous figure⁸ of 13.4 kcal mole^{-1} .

larger than that of the true cathodic curve (computed from exchange currents), and amounts to 400–500 mV. The shape of the cathodic curve is not determined by transport of indium ions in solution, since on adding NaI (0.05 M), which is known⁷ to accelerate the electrode process, the current rises approximately tenfold to a sharp diffusion-limited plateau. The shape of the cathodic polarisation curve at high enough polarisations is best interpreted by postulating the presence of a chemical stage, preceding the discharge of indium ions, and able to limit the rate of the overall cathodic process at sufficiently high negative departures from the equilibrium potential. This slow stage probably involves the conversion of hexaaquoindium ions $[\text{In}(\text{H}_2\text{O})_6]^{3+}$, the preponderant solute species, into partially hydrolysed $[\text{In}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ ions, which then take part in the electrode process⁹.

SUMMARY

1. Electrode processes on indium and thallium amalgams have been studied in solutions of their perchlorates. For thallium amalgams the rate of the process is determined, over the entire concentration range, by diffusion in the amalgam and in solution.
2. For indium amalgams the true rate of the anodic process varies linearly with potential over a wide range of potentials close to the equilibrium value. The rate of the anodic process at constant potential is directly proportional to the amalgam concentration and is independent of the concentration of the solution. The rate of the cathodic process is directly proportional to the concentration of the solution. The transfer coefficients ($\beta = 2.2 \pm 0.07$, $\alpha = 0.91 \pm 0.02$) have been calculated from the slopes of the true anodic and cathodic curves. The activation energy of the process (12.8 kcal mole^{-1}) has been computed from the temperature-dependence of the exchange current.
3. The rate of the electrode process on indium amalgam is determined by the rate of the discharge-ionisation stage over the entire range of amalgam and solution concentrations studied.

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THE CONCEPT OF ELECTRONEGATIVITY. II. AN ANALYSIS OF PAULING'S SCALE OF ELECTRONEGATIVITIES

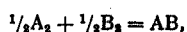
V.P. Spiridonov and V.M. Tatevskii

Our analysis¹ of the definitions of electronegativity given by different authors has shown that Pauling's definition as "the ability of atoms in a molecule to attract to themselves electrons" is devoid of physical content and is inconsistent with quantum mechanics. The present paper discusses whether it is not possible to regard his postulated equation as a definition of electronegativity, and what is the relation of the electronegativities in this equation to Pauling's definition.

In conformity with the above definition, it would be natural to try to find some property of an atom in a molecule, use of which can give a quantitative measure of this ability, in order to obtain numerical values of electronegativities. Let us now examine how numerical values of electronegativities are actually determined by Pauling's so-called thermochemical method.

Pauling's Equation

From a consideration of the quantities $\sqrt{\Delta}$, where Δ is the heat of reaction in electron-volts for a reaction of the type



Pauling² proposed the use of the equation

$$|x_A - x_B| = 0.208 \sqrt{\Delta}, \quad (1)$$

where x_A and x_B are regarded by him as the electronegativities of the univalent atoms A and B, for determining

numerical values for electronegativities. The heat of reaction for a reaction of the above type is (at $T = 0^\circ$)

$$\Delta = D(A-B) - \frac{1}{2}[D(A-A) + D(B-B)],$$

where $D(A-A)$, $D(B-B)$, and $D(A-B)$ are the dissociation energies of the corresponding molecules A_2 , B_2 , and AB , and Pauling then tacitly assumes that $\Delta > 0$, i.e. that

$$D(A-B) > \frac{1}{2}[D(A-A) + D(B-B)].$$

Later he introduces the concept of so-called normal covalent bonds[†] and the postulate that the corresponding energies are additive, stating that the energy of such a bond between the atoms A and B is equal to the arithmetic mean of the quantities $D(A-A)$ and $D(B-B)$. In conformity with this postulate, he interprets the quantity Δ as an additional "ionic portion" of the bonding energy, due to the unequal sharing of electrons between the atoms forming the bond, and he then assumes that it is a measure of the difference between the "electronegativities" of the atoms, as is indicated by Eqn. (1). In fact Eqn. (1) is the initial definition of the "electronegativities" of atoms, which is only then used by Pauling. However, it is impossible to prove that any of the quantities x_A , x_B in this equation do actually signify the ability of atoms in the molecule to attract to themselves electrons, or that they can be regarded as a measure of this "ability". On the contrary, it is clear from general theoretical considerations that the square root of any heat of reaction cannot in general be a measure of a difference in the capacities of atoms in a molecule for attracting electrons to themselves. This follows from the facts that firstly, as we have shown previously¹, the concept itself of this "ability" cannot be defined rigorously, and hence neither can a quantitative measure thereof; and secondly, even if, for example, the quantities $\bar{V}_\alpha$, defined by Eqn. (1) in Ref. 1, were introduced instead of this concept, it cannot be proved that the relation between $\bar{V}_\alpha$ and $\sqrt{\Delta}$ will be of the type postulated by Pauling's Eqn. (1).

However, it is also possible to enquire whether there exist experimental regularities of the type (1), in which x_A and x_B are some empirical constants for the given atoms A and B. Before an answer is given to this question, the following comments must be made.

It is impossible to determine unambiguously values of x_A and x_B from equations of the type (1) for different molecules (these quantities being reckoned as remaining unchanged from molecule to molecule), because the number of equations is insufficient for a unique solution. This difficulty is fundamental. Pauling tried to avoid it by assuming an arbitrary value for x_H . In fact, he took x_H for the hydrogen atom as 2.1, reckoning that elements of the first period from C to F would have "electronegativities" from 2.5 to 4.0. With this additional arbitrary hypothesis it was impossible to determine values of "electronegativities" by means of Eqn. (1), where Δ [or $D(A-A)$, $D(B-B)$, $D(A-B)$] is determined directly from experiment, for most elements in the Periodic System, since either they do not form molecules of the type A_2 or AB at all, or else energy data for such molecules are lacking. In order to find values of Δ in

[†] The concept of the "normal covalent bond" between different atoms A and B is given no clear meaning or definition by Pauling. No real bond between different atoms is a "normal covalent" bond. By this phrase Pauling probably implies some "portion" of a real bond, but it remains obscure how this "portion" can be unambiguously determined and separated.