

Integral Equations for the Distribution Function

In order to obtain the integral equations in terms of the (3,4)-approximation, it is sufficient to vary Eqn. (8) first with respect to the function $F_2^N(12)$ and then with respect to $\varphi_3^N(123)$. The integral equation for the binary distribution function has the form

$$\begin{aligned} \ln F_2^N(12) = & -\beta u(12) + \rho \int \Delta F_2^N(13) \Delta F_2^N(23) d3 + \\ & + \rho^2 \iint \Delta \varphi_3^N(134) \Delta F_2^N(23) \Delta F_2^N(24) d3 d4 + \\ & + \rho^2 \iint \Delta \varphi_3^N(234) \Delta F_2^N(13) \Delta F_2^N(14) d3 d4 + \\ & + \rho^2 \iint \Delta \varphi_3^N(134) \Delta \varphi_3^N(234) d3 d4. \end{aligned} \quad (9)$$

The triple correlation function is given by

$$\begin{aligned} \ln \varphi_3^N(123) = & \rho \int \Delta F_2^N(14) \Delta F_2^N(24) \Delta F_2^N(34) d4 + \\ & + \rho \int \Delta \varphi_3^N(124) \Delta F_2^N(34) d4 + \rho \int \Delta \varphi_3^N(234) \Delta F_2^N(14) d4 + \\ & + \rho \int \Delta \varphi_3^N(134) \Delta F_2^N(24) d4. \end{aligned} \quad (10)$$

Eqn. (9) is an obvious generalisation of Richardson's equation^{2,3} and becomes identical with it when $\Delta \varphi_3^N = 0$. With the same approximation, Eqn. (10) becomes

$$\ln \varphi_3^N(123) = \rho \int \Delta F_2^N(14) \Delta F_2^N(24) \Delta F_2^N(34) d4. \quad (11)$$

Eqn. (11) may be regarded as the simplest generalisation of the superposition approximation. This relation is simpler than the hypersuperposition approximation used by Fisher and Kopeliovich⁵. On the basis of direct topological considerations, Verlet⁴ set up a different integral equation for φ_3^N which for small ρ also reduces to approximation (11).

Both Eqns. (9) and (10) apply, regardless of density, to almost ideal gases with very weak interaction between molecules or to any system at sufficiently high temperatures. At high densities Eqn. (9) is not sufficiently accurate since it does not contain terms which would yield a correct expression for the fourth virial coefficient. In order to obtain an equation applicable to both high and low temperatures over a sufficiently wide density range, it is necessary to add to the right-hand side of Eqn. (9) appropriate terms of the order of ρ^2 :

$$\begin{aligned} & -\rho^2 \iint \Delta F_2^N(13) \Delta F_2^N(24) \Delta F_2^N(34) d3 d4 + \\ & + \frac{1}{2} \rho^2 \iint \Delta F_2^N(13) \Delta F_2^N(14) \Delta F_2^N(23) \Delta F_2^N(24) \Delta F_2^N(34) d3 d4. \end{aligned} \quad (12)$$

It is interesting to elucidate the relation between the integral equation (9) with corrections (12) and (10) and those of Fisher and Kopeliovich who used as a starting point the chain of integrodifferential equations of Bogolyubov and the hypersuperposition approximation relating the fourth-order distribution function with distribution functions of a lower order. Neglecting terms of the order of ρ^3 and higher, Bogolyubov's equation for the binary distribution function in the superposition approximation can be represented in the following form by an iteration procedure⁴:

$$\begin{aligned} \nabla_1 \ln F_2^N(12) = & -\beta \nabla_1 u(12) + \rho \int \nabla_1 \Delta F_2^N(13) \Delta F_2^N(23) d3 - \\ & - \rho^2 \iint \nabla_1 \Delta F_2^N(13) \Delta F_2^N(24) \Delta F_2^N(34) d3 d4 - \\ & - \rho_2 \iint \nabla_1 F_2^N(13) \Delta F_2^N(14) \Delta F_2^N(24) \Delta F_2^N(34) d3 d4. \end{aligned} \quad (13)$$

The equation of Fisher and Kopeliovich for F_2^N differs from the above only by an additional term on the right-hand side:

$$-\beta \rho \int \nabla_1 u(13) F_2^N(13) F_2^N(23) \Delta \varphi_3^N(123) d3. \quad (14)$$

It is easy to show that, after eliminating terms of the order of ρ^3 and higher, the result of differentiating Eqn. (9)

with correction (12) with respect to the coordinate of the first molecule, using the linearised approximation (11) and replacing the average force potential by the pair potential, is identical with Eqn. (13) plus the additional term (14). The equation of Fisher and Kopeliovich for the ternary correlation function becomes identical with our Eqn. (10) if the pair potential in the former is replaced by the average force potential and only the lowest terms involving the interaction constant are retained.

Thus at high densities and high temperatures the integro-differential equations of Fisher and Kopeliovich and the present author's integral equations give similar results, yielding in particular accurate expressions for the second, third, and fourth virial coefficients. However, it appears that the present author's equations are more accurate for small intermolecular distances.

SUMMARY

The general variational theory of molecular distribution functions² has been applied to the analysis of a special approximation assuming that second- and third-order pseudocorrelation functions are retained in the multiplicative representation of the distribution function of N particles. A system of integral equations relating second- and third-order molecular distribution functions has been obtained. At sufficiently low densities it is possible to express the ternary correlation function solely in terms of the binary distribution function (generalised superposition approximation). The relation between the equations obtained and the hypersuperposition approximation is elucidated.

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RADIOCHEMICAL AND ELECTROCHEMICAL STUDIES OF ELECTRODE PROCESSES ON AMALGAMS. IV.

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In order to determine the possible effect of diffusion processes on the kinetic parameters found by studying electrode processes on amalgams of zinc¹, thallium and indium², we shall consider the characteristics of diffusion conditions. With all amalgams at moderate concentrations

of amalgams and solutions, the anodic and cathodic polarisation curves have clear regions of limiting currents, there being a linear relationship between the anodic and cathodic limiting currents and the corresponding concentrations³. Under standard conditions of stirring (400 rev/min), the system is in a turbulent state, and the limiting current increases rapidly with rate of stirring; this is evidence of the diffusional nature of limiting currents. The thickness of the diffusion layer δ , calculated from the limiting currents using published data on diffusion coefficients, is 2.6×10^{-3} cm for diffusion in the amalgam and 2.2×10^{-3} cm for diffusion in the solution. In the case of zinc and indium amalgams, the exchange rates measured by a radiochemical method over a wide range of concentrations are considerably lower than the anodic and cathodic limiting currents; *i.e.* conditions are favourable for studying the kinetics of the electrochemical stage itself⁴; while in the case of thallium amalgam the rate of exchange is close to the anodic or cathodic limiting current at all the concentrations of amalgam and solution studied, so that diffusion processes seriously distort the results of radiochemical measurements.

Analysis of our experimental results shows that the rate of exchange between an amalgam and ions of the corresponding metal in solution, measured radiochemically, increases in the order $\text{In} < \text{Zn} < \text{Tl}$. As an illustration, the accompanying Table shows values of the exchange current for comparatively high amalgam concentrations (0.1 M) and practically identical solution concentrations†, and also transfer coefficients and energies of activation; the last column shows the free energies of hydration for the corresponding cations at infinite dilution⁵. The connection between these quantities and the exchange current will be discussed below.

Studies on the dependence of the exchange current for indium and zinc amalgams [Eqn. (1) in Ref. 2 and Eqn. (2) in Ref. 1 respectively] on solution concentration show that, in agreement with theory (Ref. 4, p. 580), the exchange current increases more slowly than linearly with increase in concentration of the corresponding ions. With thallium amalgams (Fig. 1 in Ref. 2) and with zinc amalgams at low concentrations of zinc ions (Fig. 4 in Ref. 1) there is a linear relationship between exchange rate and ionic concentration; consequently, the exchange rate is limited not

by the electrochemical stage but by the diffusion of radioactive particles in the solution. In the case of indium amalgams, the linear character of the $(\varphi - \log i_a)$ (Fig. 5, Ref. 2) and $(\varphi_{\text{eq}} - \log i_0)_{\text{Ca}}$ (Fig. 7, Ref. 2) relationships, and also the nearness of the sum of the transfer coefficients to 3, *i.e.* to the total number of electrons taking part in the electrode process, indicate that the rate of the electrode process is determined by the discharge-ionisation stage [cf. Ref. 4, Eqns. (7), (9), and (11)]. A similar conclusion can be reached for the electrode processes on a zinc amalgam, for which the theoretical relationship between exchange current and concentrations of amalgam and solution is found in the kinetic region (Ref. 1, Figs. 3 and 4), while the sum of the transfer coefficients is close to 2. In addition, in this case the normal polarisation curves agree with the theoretical ones calculated from an equation of type (16) in Ref. 4, using experimental values of exchange currents and transfer coefficients (Ref. 1, Fig. 6); this is further confirmation of our conclusion about the nature of the retarded stage and of the reliability of the values of i_0 , α , and β used in this calculation. The activation energies of the exchange process on zinc and indium amalgams are appreciably greater than that of diffusion under conditions of turbulent mixing, which, according to our results for very low concentrations of zinc amalgam¹ and the results of Fedorova and Vidovich⁶, does not exceed 5 kcal mole⁻¹. This result supports our conclusion that the rate of exchange for amalgams of zinc (in the kinetic region) and indium is limited by the electrochemical stage.

In order to elucidate the detailed mechanism of an electrode process it is necessary to know the relation between its rate, the potential, and the concentrations of amalgam and solution. For indium amalgams it has been shown, by direct measurement of the true rate of the anodic process, that at constant potential this is directly proportional to the amalgam concentration and independent of the concentration of indium ions in the solution, while the rate of the cathode process is proportional to such concentration. Furthermore, by comparing our experimental results with Eqns. (9) and (11) in Ref. 4, derived on the assumption that anodic and cathodic processes are of the first order, it is easy to show that the true rate of the cathodic process at constant potential does not depend on the amalgam concentration. Thus the overall electrode process on an indium amalgam is $\text{In} \rightleftharpoons \text{In}^{3+} + 3e$, and our results may be expressed by the equations

$$i_a = k_1 [\text{In}] e^{\beta F \varphi / RT}, \quad (1)$$

where $\beta = 2.2$, and

$$i_c = k_2 [\text{In}^{3+}] e^{-\alpha F \varphi / RT}, \quad (2)$$

where $\alpha = 0.91$. For zinc amalgams our data on the dependence of exchange current on the concentrations of amalgam and solution are insufficient for determining the order of reaction with respect to zinc for the anodic and cathodic processes. This problem was solved earlier⁷ for the same system containing additions of tetrabutylammonium sulphate; it was shown that the anodic process is a first-order reaction with respect to the amalgam concentration and is independent of the concentration of zinc ions in the solution. It can be assumed that the surface-active additive only causes a retardation of the electrode process on the zinc amalgam, without substantially affecting its mechanism, so that, in a pure solution, the reaction will also be of first

TABLE.

Amalgam	Solution	Temp., °C	α	β	$\alpha + \beta$	Exchange current, A cm ⁻²	Standard exchange current, A cm ⁻²	Activation energy, kcal mole ⁻¹	Free energy of hydration of cations at 25°, kcal x mole ⁻¹
In (0.10 M)	0.03 M In(ClO ₄) ₃ + 3 M NaClO ₄	20	0.91 ± 0.02	2.20 ± 0.07	3.11 ± 0.09	$3.1 \cdot 10^{-6}$	0.0067	12.8	-965
Zn (0.13 M)	0.025 M ZnSO ₄ + 1 M MgSO ₄	25	0.52 ± 0.04	1.40 ± 0.05	1.92 ± 0.09	$5.24 \cdot 10^{-8}$	0.11	7.4	-479
Tl (0.10 M)	0.03 M TlClO ₄ + 3 M NaClO ₄	20	~ 0.4	~ 0.6	—	$> 1 \cdot 10^{-8}$	> 0.2	2.1	-80

† As already indicated, the measured value of the exchange rate for thallium amalgam is strongly influenced by the diffusion stage. Therefore the value given in the Table must be regarded as the lower limit of the true exchange current.

order with respect to the amalgam concentration. Thus our experimental results for zinc amalgams can be represented by the equation

$$i_a = k'[Zn]e^{\beta F\phi/RT}, \quad (3)$$

where $\beta = 1.40$.

In an earlier paper⁴ it was shown, by assuming stepwise removal and addition of electrons, that comparison of the values of the transfer coefficients α and β enabled the limiting stage of an electrode process to be determined. It can be seen from the Table, which shows values of the transfer coefficients, that in the case of zinc amalgams $\beta > \alpha$ and $\beta > 1$, while for indium amalgams $\beta > \alpha$ and $\beta > 2$; only in the case of thallium amalgams are α and β approximately the same. Such a large difference between transfer coefficients for anodic and cathodic processes for metals of valency greater than unity is also found in most other electrode processes of the type $M \rightleftharpoons M^{n+} + ne$. Thus, for cadmium amalgams $\beta = 1.66$ ⁸ and $\alpha = 0.44-0.50$,^{9,10} for copper $\beta = 1.4$ and α varies from 0.38 to 0.57,¹¹⁻¹³ for nickel α varies from 0.35 to 0.7,¹³⁻¹⁵ and for cobalt $\alpha = 0.65-0.82$ ^{14,16} (all published figures have been normalised to $\alpha + \beta = 2$). For all these cases, the rate of ionisation of the metal must depend⁴ on the rate of removal of the last electron, i.e. on the rate of the stage $M^+ \rightleftharpoons M^{2+} + e$.

Let us consider this question in somewhat greater detail for an indium amalgam for which the following elementary steps can be envisaged: $In \rightleftharpoons In^+ + e$; $In^+ \rightleftharpoons In^{2+} + e$; and $In^{2+} \rightleftharpoons In^{3+} + e$ (limiting step), with the formation of the unstable intermediate ions In^+ and In^{2+} . The exchange current of the limiting step must be considerably less than for the other stages, since the true anodic ($\phi - \log i_a$) and cathodic ($\phi - \log i_c$) curves have no breaks over the whole range of potentials studied⁴. In this case the expression for the true rate of the anodic process is

$$i_a = k'[In^{2+}]e^{\beta_3 F\phi/RT}, \quad (4)$$

and taking into account the equilibrium of the two preceding steps $[In^{2+}] = k[In]e^{2F\phi/RT}$, we have

$$i_a = k[In]e^{\beta F\phi/RT}, \quad (5)$$

where $\beta = 2 + \beta_3$, i.e. $\beta > 2$. The true rate of the cathodic process is given by

$$i_c = k'[In^{2+}]e^{-\alpha_3 F\phi/RT}, \quad (6)$$

where $\alpha_3 = \alpha$, i.e. $\alpha < 1$ (since $\alpha_3 + \beta_3 = 1$). It can be seen that Eqns. (5) and (6), derived on the assumption of a retarded removal of the last electron, are in agreement with our experimental results [see Eqns. (1) and (2)]. It is not difficult to convince oneself that the assumption that removal of the first or second electron is retarded leads to relations between the transfer coefficients that contradict our experimental results. Similarly, it can be shown that, in the case of zinc amalgams, the limiting step in the electrode process is the removal of the second electron, Zn^+ ions being formed as intermediates. A study of the reaction $Zn^{2+} + 2e \rightleftharpoons Zn$ by oscillographic polarography¹⁹ and

of the anodic dissolution of zinc in perchlorate solutions¹⁸ apparently indicates the possible formation of these ions⁵.

Considering that the closest analogue to indium in Mendeleev's Periodic System is thallium, it is interesting to compare our data on indium amalgams with the results of studies on the oxidation-reduction mechanism of the reaction $Tl^+ \rightleftharpoons Tl^{3+} + 2e$. Analysis of the anodic and cathodic polarisation curves, obtained on a platinum electrode²³, has shown that this process consists of two consecutive one-electron steps with different exchange currents, that of the step $Tl^{2+} \rightleftharpoons Tl^{3+} + e$ being lower than that of the step $Tl^+ \rightleftharpoons Tl^{2+} + e$. This mechanism is closely similar to that proposed by us for indium. It is interesting that, for homogeneous isotopic exchange in the $Tl^+ - Tl^{3+}$ system in $NaClO_4$ solutions, which evidently proceeds by a stepwise mechanism with formation of Tl^{2+} ions, the activation energy is ~ 15 kcal mole⁻¹,²⁴ i.e. extremely close to that found by us for exchange on indium amalgams and very different from that for thallium amalgams (see Table). Taking into account the similarity between the energies of activation of an oxidation-reduction reaction on an electrode and in the bulk of the solution²⁵, it may be supposed that the high energy of activation found by us for indium corresponds to the removal of the third electron, whereas the activation energy of the step $In \rightleftharpoons In^+ + e$ is very low (similar to the activation energy of the reaction $Tl \rightleftharpoons Tl^+ + e$). The sharp difference between the slopes of the anodic and cathodic polarisation curves (corresponding to the condition $\beta > \alpha$) for the oxidation-reduction process $Sn^{2+} \rightleftharpoons Sn^{4+} + 2e$ on a flowing mercury electrode²⁶ also indicates that it is a stepwise process with the reaction $Sn^{3+} \rightleftharpoons Sn^{4+} + e$ as the limiting step.

Consideration of the Table and of the published data for other metals shows clearly the tendency towards diminution of exchange current with increase in valency of the cation, with a simultaneous sharp increase in the activation energy of the electrode process and in the free energy of hydration of the cations¹. Comparison of the energies of hydration of the ions of an element having different states of oxidation ($Cu^+ - Cu^{2+}$; $Fe^{2+} - Fe^{3+}$; $Tl^+ - Tl^{3+}$; $Ce^{3+} - Ce^{4+}$, etc.) shows that increasing the charge on the cation causes a sharp rise in hydration energy; it is well known that this rise is greater, per unit increase in charge, the greater the initial charge on the cation⁵. Although the activation energy forms only a negligible part of the hydration energy of the corresponding cations, it can be assumed to be due, to a considerable extent, to rearrangement of the hydration envelope when the charge on the reacting particle changes. Thus, the fact that in the stepwise electrode process $M \rightleftharpoons M^{n+} + ne$ the limiting step is the reaction $M^{(n-1)+} \rightleftharpoons M^{n+} + e$ is evidently explained by the very great difference in the hydration energies of the cations taking part in the latter reaction, whereas for the other steps this difference must be considerably less. Since univalent ions (Tl^+ , Ag^+ , etc.) are

§ The idea of the stepwise transfer of electrons in electrode reactions on amalgam electrodes and the possibility of determining the limiting step by analysis of the relation between the transfer coefficients was developed for zinc amalgams⁷ and worked out by us in greater detail for indium amalgams²². Similar conclusions were drawn from analogous considerations in later work by Bockris *et al.*¹² and by Gerischer and Pérez-Fernández²⁰. The possibility of similarly explaining a marked difference in transfer coefficients was shown by Randles²¹.

¶ The existence of such a relation between exchange currents on amalgam electrodes and the solvation energies of the corresponding cations was first shown by Pleskov and Miller²⁷.

† A study of the oxidation-reduction potentials and reducing properties of the $In-In^{3+}$ system¹⁷ indicates that In^+ and, apparently, In^{2+} ions are formed in aqueous solutions. In^+ ions are also formed in the anodic polishing of indium in perchlorate solutions¹⁸.

weakly hydrated, the step $M \rightleftharpoons M^+ + e$ has, of course, insignificant activation energy, and, therefore, in comparison with the subsequent electrochemical steps, it is practically an equilibrium process.

Theoretical calculations of the activation energies for the discharge of bivalent ions on the corresponding solid metals²⁸ confirm the idea of stepwise discharge-ionisation of metals. These calculations show that the direct discharge of bivalent ions requires a much greater activation energy than a stepwise process involving the formation of intermediate univalent ions.

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SUMMARY

1. On the assumption of stepwise discharge-ionisation on metal electrodes, it is concluded from the relation between transfer coefficients for zinc and indium amalgams that the rate of the discharge-ionisation reaction is limited by the removal (or addition) of the final electron $M^{(n-1)+} \rightleftharpoons M^{n+} + e$.
2. It is suggested that the exchange currents and activation energies for the discharge-ionisation of cations of metals having variable valency are related to the difference in free energy of hydration between oxidised and reduced forms of the metal involved in the limiting step of the process.

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THE "CORRESPONDENCE CURVES" OF THE HETEROGENEOUS LIQUID REGION OF TERNARY SYSTEMS

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We have applied the term "correspondence curve"¹ to the curve relating the physical properties of the conjugate phases in the heterogeneous liquid region. A correspondence curve can be plotted both for one and for several different physical properties of such phases. Each tie-line is characterised by a single value of the chosen physical property of each constituent phase, and therefore it is represented by a single point on the correspondence curve. A succession of such points constitutes the correspondence