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Chemistry. — *"On the introduction of the conception of the solubility of metal ions with electromotive equilibrium."* By Dr. A. Smits. (Communicated by Prof. H. W. Bakhuis Roozeboom).

(Communicated in the meeting of April 27, 1906.)

If a bar of NaCl is placed in pure water or in a dilute solution, the NaCl-molecules will pass into the surrounding liquid, till an equilibrium has been established; then the molecular thermodynamic potential of the Na Cl in the bar has become equal to that of the Na Cl in the solution.

As known, this equilibrium of saturation, represented by the equation:

$$\mu_{\mathrm{NaCl}} = \mu'_{\mathrm{NaCl}}$$

is characterized by the fact that per second an equal number of molecules pass from the bar into the solution, as from the solution into the bar.

We shall call this equilibrium a purely chemical equilibrium. It is true that in solution the Na Cl-molecules split up partially into particles charged either with positive or negative electricity, which are in equilibrium with the unsplit molecules, but for the heterogeneous equilibrium solid-liquid under consideration this is not of *direct* importance.

If, however, we immerge a metal e. g. Zn into a solution of a salt of this metal, e. g. $ZnSO_4$, we observe a phenomenon strongly deviating from the one just discussed, which according to our present ideas may be accounted for by the fact that a metal does not send out into the solution *electrically neutral* molecules as a salt, but exclusively *ions with a positive charge.*

If the particles emitted by the bar of zinc were *electrically neutral,* then the zinc would continue to be dissolved till the molecular thermodynamic potential of the zinc in the bar of zinc had become equal to that of the zinc in the solution, in which case the equation:

$$\mu_{zn} = \mu'_{zn}$$

would hold.

This, however, not being the case, and the emitted Zn-particles being electro-positive, an equilibrium is reached *long* before the thermodynamic potential of the zinc-particles with the positive electric charge in the solution has become equal to that of the zinc in the bar of zinc with the negative electric charge. That in spite of this an equilibrium is possible, is due to the fact that an electrical phenomenon acts in conjunction with the chemical phenomenon.

The zinc emitting positive *Zn*-ions, the surrounding solution becomes electro-positive, and the zinc itself electro-negative. As known, this gives rise to the formation of a so-called electric double-layer in the bounding-layer between the metal and the electrolyte, consisting of positive *Zn*-ions on the side of the electrolyte and an equivalent amount of negative electricity or electrons in the metal.

By the formation of this electric double-layer an electric potential difference between metal and electrolyte is brought about, which at first increases, but very soon becomes constant. This takes place when the potential difference has become great enough to prevent the further solution of the *Zn*-ions.

In order to compute the potential difference between the metal and the solution, we shall apply the principle of the virtual displacement, as has been done before by Mr. VAN LAAR.[1]

If we have to do with a purely chemical equilibrium then with virtual displacement of this equilibrium the sum of the changes ot molecular potential will be $=0$, which is expressed by the equation of equilibrium:

$$\Sigma(\mu_1\, dn_1) = 0.$$

If the equilibrium is a purely electrical equilibrium then with a virtual displacement of this equilibrium the sum of the changes of electric energy will be $=0$.

If however we have an equilibrium that is neither purely chemical, nor purely electrical, but a combination of the two, as is the case with electromotive equilibrium, then with virtual displacement of this equilibrium, the sum of the changes of the molecular-potential $+$ the sum of the changes of the electric energy will have to be $=0$.

If we represent the mol. potential of the *Zn*-ions by $\overset{+}{\mu}_{zn}$ in case of electromotive equilibrium, we know that $\overset{+}{\mu}_{zn}$ is *much* smaller than μ_{zn} or the mol. potential of the zinc in the bar of zinc.

If we now suppose that a *Zn*-ion emitted by the zinc virtually carries a quantity of electricity de from the metal towards the solution, then this quantity of electricity being carried by a ponderable quantity $\frac{de}{\nu\varepsilon}$ when $\nu =$ valency of the metal and $\varepsilon =$ the charge of a univalent ion, the increase of the thermodynamic potential during this process will be equal to

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[1] Chem. Weekbl. N°. 41, 1905.

$$\frac{\overset{+}{\mu}_{zn} - \mu_{zn}}{\nu \varepsilon}\, de$$

which increase is negative, because $\mu_{zn} > \overset{+}{\mu}_{zn}$.

In the virtual displacement of the quantity of electricity *de* from the metal towards the solution the change of the thermodynamic potential is not the only one that has taken place during this process.

If we call the electric potential of the solution V_e and that of the zinc V_m, we know that in the above case $V_e > V_m$ and $V_e - V_m = \Delta$ indicates the potential difference of the electrolyte and the metal. With the virtual displacement of the quantity of electricity *de* from the metal to the electrolyte this quantity has undergone an electrical potential increase Δ, and so the electric energy has increased with $\Delta\, de$.

From the principle of virtual displacement follows that with electromotive equilibrium

$$\frac{\overset{+}{\mu}_{zn} - \mu_{zn}}{\nu \varepsilon}\, de + \Delta\, de = 0, \quad \ldots\ldots\ldots \quad (1)$$

or

$$\Delta = - \frac{\overset{+}{\mu}_{zn} - \mu_{zn}}{\nu \varepsilon} \quad \ldots\ldots\ldots \quad (2)$$

Now we know that the mol. thermodyn. potential of a substance may be split up as follows:

$$\mu = \mu' + R\,T \ln C$$

where in diluted states of matter μ' may be called a function of the temperature alone.

In non-diluted states however, μ' depends also somewhat on the concentration.

If we now apply this splitting up also to equation (2), we get:

$$\Delta = - \frac{(\overset{+}{\mu'}_{zn} - \mu_{zn}) + R\,T \ln C}{\nu \varepsilon} \quad \ldots\ldots \quad (3)$$

where C represents the concentration of the *Zn*-ions in the electrolyte.

If we now put:

$$\frac{\mu_{zn} - \overset{+}{\mu'}_{zn}}{R\,T} = \ln K \quad \ldots\ldots\ldots \quad (4)$$

we may say of this K that for diluted states of matter it will only depend on the temperature, and will therefore be a constant at constant temperature.

From equation (3), (4) follows

$$\Delta = \frac{RT}{\nu\varepsilon} \ln \frac{K}{C} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (5)$$

Mr. VAN LAAR already pointed out that this equation, already derived by him in the same way is identical with that derived by NERNST $\Delta = \frac{RT}{\nu\varepsilon} \ln \frac{P}{p}$, in which therefore $\frac{P}{p}$ stands instead of $\frac{K}{C}$. P represents the "elektrolytische Lósungstension" of the metal, and p the "osmotic pressure" of the metal-ions in the solution.

Rejecting the osmotic phenomenon as basis for the derivation of the different physico-chemical laws, we must, as an inevitable consequence of this, also abandon the osmotic idea "elektrolytische Lósungstension" introduced by NERNST.

The principal purpose of this paper is to prove that there is not any reason to look upon this as a disadvantage, for, when we seek the physical meaning of the quantity K in equation (5), it can be so simply and sharply defined; that when we take the theory of the thermodynamic potential as foundation, we do not lose anything, but gain in every respect.

In order to arrive at the physical meaning of the quantity K, we put for a moment

$$C = K$$

from which follows

$$\Delta = 0.$$

From this follows that there is a theoretical possibility to give such a concentration to the metal-ions in a solution that when we immerge the corresponding metal in it, *neither the metalnor the solution gets electrically charged.*

How we must imagine this condition is shown by equation (2). Let us put there $\Delta = 0$, then follows from this for an arbitrary metal

$$\mu_m = \overset{+}{\mu}_m$$

or in words the molecular potential of the metal in the bar is equal to that of the metal-ions in the solution.

So it appears that we have here to do with an equilibrium which is perfectly comparable with that between the Na Cl in the bar Na Cl, and the salt in the solution.

The only difference is this that the molecules of a salt in solution are neutrally electric, whereas the metal particles in solution are charged with positive electricity, hence the physical meaning of the equation $\mu_m = \overset{+}{\mu_m}$ is simply this that in *absence* of a potential difference, per second an equal number of metal particles are dissolved as there are deposited.

If we express this in the most current terms, we may say, that when $C = K$ the metal-ions have reached their *concentration of saturation,* and that K therefore represents the *solubility of the metal-ions.*

To prevent confusion, it will be necessary to point out that the fact that the dissolved metal-particles in equilibrium with the solid metal have an electric charge, is attended by peculiarities which are met with in no other department.

Thus it will appear presently that in every solution of copper-sulphate which is not extremely diluted, the concentration of the copper-ions is supersaturated with respect to copper. Yet such a copper-sulphate-solution is in a perfectly stable condition, because the copper-ions constitute a part of the following homogeneous equilibrium,

$$CuSO_4 \rightleftarrows Cu^{\cdot\cdot} + SO_4''$$

which is perfectly stable as long as the solution is unsaturate or is just saturate with $CuSO_4$-molecules.

If we now, however, insert a copper bar into the solution, the condition changes, because the Cu-ions which were at first only in equilibrium with the $CuSO_4$-mols and with the SO_4''-ions, must now also get into equilibrium with the copper bar, and, the concentration of the Cu-ions with respect to copper being strongly supersaturate, the Cu-ions will immediately deposit on the copper, till the further depositing is prevented in consequence of the appearance of a double layer.

We shall further see that in the most concentrated solution of a zinc-salt the concentration of the zinc-ions always remains below the concentration of saturation, which appears immediately when we immerge a zinc-bar into such a solution; the zinc emits zinc particles with a positive charge into the solution, till the appearance of the electric double layer puts a stop to the phenomenon of solution.

In order to find the values of K for different metals we make use of the observed potential difference with a definite value of C, We know the potential difference at 18° and with normal concentration of the ions; i. e. when solutions of 1 gr. aeq. per liter of water are used. These potential differences are called electrode potentials, and will be denoted here by Δ_o.

If we express the concentration in the most rational measure, viz. in the number of gr. molecules dissolved substance divided by the total number of gr. molecules, we may write for the concentration of 1 gr. eq. per liter

$$\frac{1}{55{,}5\,v + 1}$$

in which v represents the valency of the metal. In this it has been further assumed, that the dissociation is total, and the association of the water molecules has not been taken into account.

If we now write the equation for the electrode potential of an arbitrary metal, we get:

$$\Delta_0 = \frac{RT}{v\varepsilon}\, ln \frac{K}{\frac{1}{55{,}5\,v + 1}}$$

or

$$\Delta_0 = \frac{RT}{v\varepsilon}\, ln\, K(55{,}5\,v + 1)$$

If we use ordinary logarithms for the calculation, we get:

$$\Delta_0 = \frac{RT}{v\varepsilon \times 0{,}4343}\, log\, K(55{,}5\,v + 1)$$

If we now express R in electrical measure, then

$$\Delta_0 = \frac{0{,}000198}{v}\, T\, log\, K(55{,}5\,v + 1)$$

and for $t = 18$ or $T = 291°$

$$\Delta_0 = \frac{0{,}0578}{v}\, log\, K(55{,}5\,v + 1)$$

If we now calculate the quantity $log\,K$ by means of this equation from the observed values of Δ_0, we get the following. (See table p. 8).

In the succession in which the metals are written down here, the value of Δ_0 decreases and with it the value of $log\,K$.

For the metals down to *Fe* (*Fe* included) $log\,K$ is greater than zero, so K greater than 1.

Now we know that C for a solution is always smaller than 1; hence K will always be larger than C for the metals mentioned, and as K denotes the concentration of saturation of the metal-ions, Values of *log K* at 18°.

metal ion	Δ0	*log K*	metal ion	Δ0	*log K*
$K^{\cdot}$	(+ 2,92) [1]	(+48,77)	$Co^{\cdot\cdot}$	— 0,045	— 1,805 2
$Na^{\cdot}$	(» 2,54)	(42,19)	$Ni^{\cdot\cdot}$	» 0,049	— 1,872 × 2
$Ba^{\cdot\cdot}$	(» 2,54)	(42,92 × 2)	$Sn^{\cdot\cdot}$	< » 0,085	<— 2,49 × 2
$Sr^{\cdot}$	(» 2,49)	(42,06 × 2)	$Pb^{\cdot}$	» 0,13	— 3 27 × 2
$Ca^{\cdot}$	(» 2,28)	(38,42 × 2)	$H^{\cdot}$	» 0,28	— 6,6
$Mg^{\cdot}$	» 2,26	38,07 × 2	$Cu^{\cdot\cdot}$	» 0,61	— 11,58 × 2
$Al^{\cdot\cdot}$	» 1,00	16,56 × 3	$Bi^{\cdot\cdot\cdot}$	< » 0,67	<— 12 33 × 3
$Mn^{\cdot\cdot}$	» 0,80	12,81 × 2	$Hg_2^{\cdot\cdot}$	» 1,03	— 18,84 × 2
$Zn^{\cdot\cdot}$	» 0,49	7,45 × 2	$Ag^{\cdot}$	» 1,05	— 19,92
Cd	» 0,14	1,39 × 2	$Pd^{\cdot}$	» 1,07	— 19,03 × 2
$Fe^{\cdot}$	» 0,063	0,065 × 2	$Pt^{\cdot\cdot\cdot\cdot}$	» 1,14	— 20,62 × 4
$Tl^{\cdot}$	» 0,045	— 0,245 × 2	$Au^{\cdot\cdot}$	» 1,36	— 26,27 × 3

the metal-ions will not yet have reached their concentration of saturation even in the most concentrated solutions of the corresponding metal-salts. Hence, when the corresponding metal is immerged, metal ions will be dissolved, in consequence of which the solution will be charged with positive and the metal with negative electricity.

Theoretically the case, in which K would always be smaller than C, can of course not occur. If $\log K$ is smaller than zero, so K smaller than 1, then the theoretical possibility is given to make the potential difference between the metal and the corresponding salt solution reverse its sign, which reversal of sign of course takes place through zero. Whether it will be possible to realize this, depends on the solubility of the salt.

If we now take the metal copper as an example, we see that for this metal K has the very small value of 10^{-23}. On account of this very small value of K, C is greater than K in nearly all copper-salt-solutions, or in other words the concentration of the *Cu*-ions is greater than the concentration of saturation. Hence copper-ions are deposited on a copper bar, when it is immerged, in consequence which the bar gets charged with positive, and the solution with negative electricity.

But however small K may be, it will nearly always be possible to make C smaller than K. In a copper-salt-solution e.g. this can very easily be done, as is known, by addition of KCN, which in consequence of the formation of the complex-ions $[Cu_2(CN)_4]''$, causes copper-ions to be extracted from the solution. The solution, which at first had a negative charge compared with the metal copper, loses this charge completely by the addition of KCN, and receives then a positive charge.

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[1] The values of Δ_0 between parentheses have been calculated from the quantity of heat.

In the above I think I have demonstrated the expediency of replacing the vague idea "elektrolytische Lösungs-tension" by the sharply defined idea solubility of metal ions.

Amsterdam, April 1906. *Anorg. Chem. Lab. of the University.*

Physics. — *"On the course of the P, T-curves for constant concentration for the equilibrium solid-fluid."* By Dr. A. Smits. (Communicated by Prof. J. D. van der Waals.)

(Communicated in the meeting of April 27, 1906).

In connection with my recent investigations it seemed desirable to me to examine the hidden connection between the sublimation and melting-point curves for constant concentration, more particularly when the solid substance is a dissociable compound of two components. This investigation offered some difficulties, which I, however, succeeded in solving by means of data furnished by a recent course of lectures giving by Prof. van der Waals. Though his results will be published afterwards, Prof. van der Waals allowed me, with a view to the investigations which are in progress, to use that part that was required for my purpose.

In his papers published in 1903 in connection with the investigation on the system ether-anthraquinone [1]) van der Waals also discussed the P, T-lines for constant x for the equilibrium between solid-fluid [2]), and more particularly those for concentrations in the immediate neighbourhood of the points p and q, where saturated solutions reach their critical condition.

Then it appeared that the particularity of the case involved also particularities for the P, T-line, so that the course of the P, T-line as it would be in the usual case, was not discussed.

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[1]) These Proc. VI p. 171 and p, 484 Zeitschr. f. phys. Chem. **51**, 193 and **52**, 587 (1905).

[2]) These Proc. VI p. 230 and p. 357.