

THEORY OF THE GLASS ELECTRODE. IX. APPLICATION OF ION-EXCHANGE THEORY TO GLASS ELECTRODES FUNCTIONING AS DIFFERENT METAL ELECTRODES

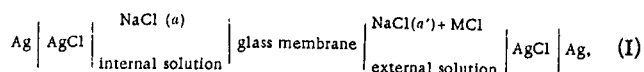
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During the past fifty years a large amount of experimental data has accumulated on the behaviour of the glass electrode as a hydrogen electrode and also on its conversion to a sodium electrode.

A number of investigations,¹⁻⁷ including our own, confirm that glass electrodes are able, as a result of exchange of hydrogen and sodium ions from the glass for cations from the solution, to acquire a new electrode function, determined by a cation not originally present in the glass.

The extension of the fundamental ideas of ion-exchange theory⁸ to this change in behaviour of glass electrodes is of considerable theoretical interest. The aim of the present work was to attempt a quantitative check of the agreement between ion-exchange theory and experimental results obtained for the conversion of the glass electrode from a sodium to a hydrogen electrode and also to potassium and lithium electrodes.

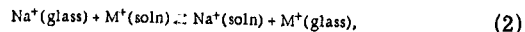
As we have already shown,⁷ the e.m.f. of the galvanic cell



calculated on the basis of ion-exchange theory, can be represented in the following form for a soda glass:

$$E_T = 0 \log \frac{K a_{\text{NaCl}}}{a_{\text{MCl}} + K a_{\text{NaCl}}} + \varphi_{\text{as}} \quad (1)$$

where a_{NaCl} is the activity of the internal electrolyte solution containing the principal* ion, a_{NaCl} the activity of the external electrolyte solution containing the principal ion, a_{MCl} the activity of the second electrolyte MCl in the external solution, K the equilibrium constant for the exchange reaction



$\theta = 2.3 RT/F$, and φ_{as} is the asymmetry potential.

Taking the difference between two values of E_T for two mixed solutions, in which the activities of MCl and NaCl are a' and a'' , and simplifying, we obtain

$$\Delta E_T = \theta \log \frac{a'_{\text{MCl}} + K a'_{\text{NaCl}}}{a''_{\text{MCl}} + K a''_{\text{NaCl}}} \quad (3)$$

or

$$\Delta E_T = \theta \log \frac{m_{\text{MCl}}(m_{\text{MCl}} + m'_{\text{NaCl}}) \gamma_{\pm \text{MCl}}^2(\text{NaCl}) + K m'_{\text{NaCl}}(m'_{\text{NaCl}} + m_{\text{MCl}}) \gamma_{\pm \text{NaCl}}^2(\text{MCl})}{m_{\text{MCl}}(m_{\text{MCl}} + m''_{\text{NaCl}}) \gamma_{\pm \text{MCl}}^2(\text{NaCl}) + K m''_{\text{NaCl}}(m''_{\text{NaCl}} + m_{\text{MCl}}) \gamma_{\pm \text{NaCl}}^2(\text{MCl})} \quad (4)$$

From this formula we calculated the theoretical change in e.m.f. ΔE_T produced by replacing one mixed solution having the concentration $m'_{\text{NaCl}} = 1$ in galvanic cell (I) by another mixed solution in which the NaCl concentration is m'' but the MCl concentration is the same as in the previous solution. For this calculation it is necessary to know not only the corresponding concentrations and exchange constants calculated from the experimental data but also the activity coefficients of MCl in the presence of NaCl ($\gamma_{\pm \text{MCl}}(\text{NaCl})$), and also $\gamma_{\pm \text{NaCl}}(\text{MCl})$.

For solutions of NaCl + HCl we took these data from Harned's paper.⁹ For NaCl + KCl and NaCl + LiCl we calculated the activity coefficients by the method of Nikol'skii and Rabinovich.¹⁰

The calculated values were compared with the experimental values of ΔE for galvanic cell (I): $\Delta E = E' - E''$, E' being the e.m.f. when the NaCl concentration in the external solution is unity. The glass electrodes employed in the experiments were made of sodium aluminoborosilicate glasses of the following compositions:

No. 1 75% SiO₂, 3% Al₂O₃, 11% B₂O₃, 11% Na₂O,

No. 2 71% SiO₂, 3% Al₂O₃, 11% B₂O₃, 15% Na₂O.

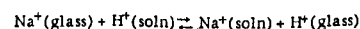
The Table* gives ΔE and calculated values for solutions of NaCl + HCl ($m_{\text{HCl}} = 0.01$) at different temperatures.

In the calculation of ΔE_T the expression $\theta \log (a'_{\text{HCl}} + K a'_{\text{NaCl}}) = \text{constant}$, in the numerator of equation (4), was always taken as constant for a given temperature and corresponded to a standard mixed solution in which the molality of the sodium chloride was unity, but $m_{\text{HCl}} = 0.01$.

m_{NaCl}	20° ($K = 0.40$)		35° ($K = 0.51$)		50° ($K = 0.60$)		65° ($K = 0.69$)	
	ΔE	ΔE_T	ΔE	ΔE_T	ΔE	ΔE_T	ΔE	ΔE_T
1.0	—	—	—	—	—	—	—	—
0.5	34	38	35	35	—	36.3	38	37
0.1	94	102	105	107	109	114	118	119
0.05	119	128	130	138	138	148	150	150
0.03	137	145	148	154	159	163	174	169
0.01	167	174	—	183	193	196	203	206
0.006	177	183	188	193	203	208	216	219
0.003	186	191	196	202	213	215	224	229
0.001	195	198	209	209	220	218	232	231

By plotting ΔE_T [$\Delta E_T = \theta \log (a_{\text{HCl}} + K a_{\text{NaCl}}) + \text{const}$] as abscissae and the experimental ΔE as ordinates, the two sets of values may be compared accurately.

The simple ion-exchange theory,⁸ on the basis of which we deduced equation (4) and calculated the constants K , assumes that the strength of all the bonds linking hydrogen ions with the silicate lattice of the glass is the same; i.e. the exchange reaction



is characterised by a single equilibrium constant. If the glass electrode follows closely the simple ion-exchange theory, then the $\Delta E = f(\Delta E_T)$ plots should give a straight

* By "principal" ion we mean the potential-determining ion originally contained in the glass.

* The values of the constants K employed for the calculation of ΔE_T are given in parentheses after the values of the temperature.

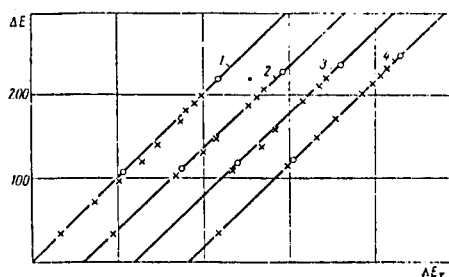


Fig. 1. $\Delta E = f(\Delta E_T)$ for the transition of the glass electrode from a sodium electrode to a hydrogen electrode.

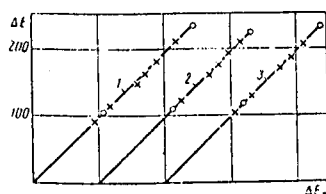


Fig. 2. $\Delta E = f(\Delta E_T)$ for the transition of the glass electrode from a sodium to a potassium electrode:

1) 20°; 2) 35°; 3) 50°.

line with a unit slope in the region where the electrode is acting as a sodium electrode, in the transition region, and where it is acting as an M^+ electrode.

Any deviation from the simple ion-exchange theory should be shown on the $\Delta E = f(\Delta E_T)$ diagram by the experimental points lying outside the straight line.

If the divergence from simple ion-exchange theory is observed only in that region of the abscissae in which the electrode is passing from a sodium electrode to an M^+ electrode, then deviations should certainly be observed there, but above and below this transition region, i.e. where there is a purely hydrogen or a purely sodium electrode, the experimental points should lie on the same straight line.

A difference should be noted between the $\Delta E = f(\Delta E_T)$ plots under discussion and the $\Delta E = f(\Delta E_p)$ curves given in our previous paper.⁶

The quantity*

$$\Delta E_p = 0.1 \log \frac{a_{NaCl}}{a_{NaCl}} \quad (5)$$

was calculated on the assumption that the glass membrane behaved as an ideal sodium electrode in galvanic cell (I) and consequently a linear relation between ΔE and ΔE_p was obtained only in the region where the sodium electrode was maintained. With this condition

$$\Delta E = \Delta E_T = \Delta E_p \quad (6)$$

* Calculation of ΔE_p was carried out for the same mixed solutions of NaCl + HCl, NaCl + KCl, and NaCl + LiCl, for which the values of ΔE_T have been calculated in the present work.

In the transition region between the sodium and M^+ electrodes, if the glass electrode follows simple ion-exchange theory, then

$$\Delta E = \Delta E_T = \Delta E_p \quad (7)$$

If the simple theory is not followed in the transition region, then

$$\Delta E \neq \Delta E_T \neq \Delta E_p$$

In the region in which the electrode has completely acquired its new function (M^+ electrode), according to the ion-exchange theory of the glass electrode the relationship

$$\Delta E = \Delta E_T = \Delta E_p \quad (8)$$

should also be satisfied.

Fig. 1 shows plots of $\Delta E = f(\Delta E_T)$ for experiments with mixed solutions of sodium and hydrogen chlorides at 20°, 35°, 50°, and 65°. The circles denote data for pure NaCl solutions and the crosses data for mixed solutions.

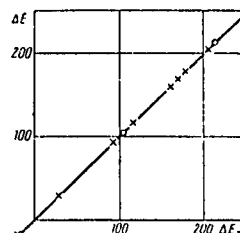


Fig. 3. $\Delta E = f(\Delta E_T)$ for the transition of the glass electrode from a sodium to a lithium electrode at 20°.

The points which correspond to a pure sodium electrode or a pure hydrogen electrode lie satisfactorily on a straight line at all the temperatures which we have investigated.

In the transition region between sodium and hydrogen electrodes at 20°, 35°, and 50° divergencies are observed between the values of ΔE and ΔE_T , which reach 8–10 mV at 20°, but do not exceed 4–6 mV at higher temperatures. At 65° the deviations are practically absent.

The generalised ion-exchange theory¹¹ explains the divergence between theoretical and experimental data in the transition region on the assumption that there are different types of bond between the hydrogen ions and the silicate anions of the glass.

The exchange reactions of these differently bound hydrogen ions with sodium ions from the solution will differ in the value of the exchange constants. In calculating ΔE , we used a simple theory which envisaged a single exchange constant for each ion-exchange reaction between glass and solution. The deviations from the curves in the transition region for experiments with solutions of NaCl + HCl show that, in the soda glasses examined by us, hydrogen ions form more than one type of bond. It can be supposed that raising the temperature levels out the differences in the exchange constants for the different groups of hydrogen ions and as a result the experimental curves obtained at 65° give good agreement between experimental data and ion-exchange theory.

Using equation (4) to calculate ΔE , in the experiments with mixed solutions of NaCl + KCl and NaCl + LiCl, i.e. for transition from sodium to potassium and from sodium to lithium electrodes, we compared the calculated values ΔE , with the experimental values ΔE .

The results are shown in Figs. 2 and 3 from which it can be seen that, for the transition from a sodium to a potassium or a lithium electrode, the $\Delta E = f(\Delta E_0)$ curves show either no deviations of ΔE from ΔE_0 , at all in the transition region or else such deviations are very small (≤ 3 mV) and are observed only over a short section of the curve.

The fact that, in the transition from a sodium to a lithium electrode (and also to a potassium electrode at 50°), no deviations are observed enables us to assume that, from the point of view of ion-exchange theory, the bonds linking the sodium, potassium, and especially lithium ions to the silicate lattice of the glass are equivalent.

SUMMARY

1. The results of an experimental investigation of glass electrodes made of sodium aluminoborosilicate glasses, published in earlier papers,^{6,7} are discussed from the point of view of the simple ion-exchange theory of the glass electrode. The simple theory is confirmed within experimental error for the transition of glass electrodes from sodium to potassium and lithium electrodes.
2. Certain deviations of the experimental results from the theoretical in the transition region for the exchange of sodium ions from the glass with hydrogen ions from the solution can be explained in terms of the generalised ion-exchange theory,¹¹ both here and for glass ES-1, by the lack of energetic equivalence between the bonds linking individual groups of hydrogen ions in the glass.
3. It was not possible on the basis of previous investigations^{8,11} to decide unequivocally whether the lack of equivalence between the bonding of different groups of ions holds only for hydrogen ions or whether it holds also for metallic ions. Our data show that the transition of a glass electrode from one metallic electrode to another conforms to the simple ion-exchange theory also in the transition region; i.e. all ions of a given alkali metal in the glass are energetically equivalent, in contrast to hydrogen ions.

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EFFECT OF STRUCTURE ON THE THERMAL CONDUCTIVITY OF POLYMERS

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In recent years much work has been done on the characteristics of the amorphous and crystalline states of polymers as affected by molecular structure, chain flexibility, and interchain forces.¹⁻⁶ The effect of the phase constitution of polymers on their mechanical properties has been discussed in general terms.⁷ However, little has been published on the effect on their thermal conductivity. Kargin et al.⁸ give merely a general indication of the dependence of physical parameters of polymers, including their thermal conductivity, on their phase constitution.

In polymers, as in other non-metallic substances, the conduction of heat is to be regarded as an aggregate result of the vibrational motion of the molecules, a peculiarity of which in this case is the presence of long flexible chains. In the presence of a temperature gradient in the polymer, vibrational energy is transferred from a point at a higher temperature to a point at a lower temperature. Increase in temperature in the polymer leads to a weakening of the bonds between the active macromolecules and increases their mobility.

The present investigation was concerned with the relation between the thermal conductivity of polymers and their physical structure and phase constitution.

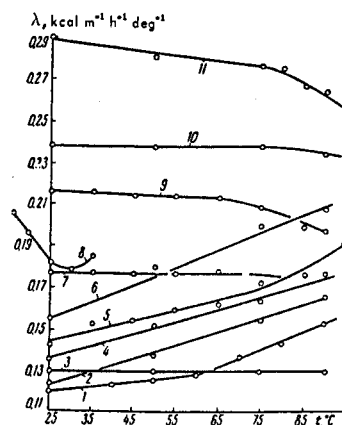


Fig. 1. Variation of thermal conductivity of polymers with temperature.

EXPERIMENTAL

The thermal conductivity of polymers was investigated over a wide range of temperatures by the non-steady-state thermal method worked out by Kondrat'ev.⁹ The plane bicalorimeter method¹⁰ was used also.

Among amorphous polymers the following were investigated (Fig. 1): polystyrene (5), bitumen (1), epoxide (6), MBC (copolymer of butyl methacrylate and dimethacrylic ester of triethylene glycol) (3), polyurethanes K-30 and K-31