first period is shown in Table 1. It is seen that the ionisation *increases* during auroræ and also with their extension to the southern part of the sky. The material of the first period is unfortunately not great, but the indication in Table 1 of an increase of the ionisation during auroræ is strongly supported by the similar increase of the ionisation during magnetic disturbances in the same period, which was shown in an earlier paper[2].

Table 1.

Extension over the sky	Clear sky, no aurora	Homogeneous arcs	Arcs with rays	Diffuse surfaces	Pulsating aurora	All types
Northern sky	2·68(12)	2·74(11)	2·79(7)	2·95(1)	3·12(1)	2·79(20)
Southern sky		2·83(8)	2·83(19)	2·79(7)	2·88(7)	2·83(41)
	2·68(12)	2·78(19)	2·82(26)	2·81(8)	2·91(8)	(61)

The numbers are pairs of ions/c.c./sec. in air of 1 atm. pressure.
The numbers within parentheses are numbers of records.

A catalogue of 757 observations of auroræ boreales (1,134 noted auroral phenomena), carried out mainly at Abisko from the end of August 1932 to the end of March 1933, will be published elsewhere[3], and the catalogue contains also the simultaneously recorded values of the ionisation in the Steinke apparatus. Some results of the comparison between simultaneous auroral observations and records of ionisation are briefly collected in Table 2; further results are found in the above mentioned catalogue.

Table 2.

Height of auroræ in the sky	Shield open upwards		Closed shield	
	Intensity of auroræ $\geqslant 0{\cdot}5$	$\geqslant 2$	Intensity of auroræ $\geqslant 0{\cdot}5$	$\geqslant 2$
0° N–60° N	2·783(174)	2·783(127)	1·944(63)	1·945(48)
60° N–60° S	2·780(78)	2·770(53)	1·942(33)	1·937(20)
60° S– 0° S	2·774(59)	2·769(28)	1·933(16)	1·928(12)
During clear sky and no aurora	2·787(66)		1·956(56)	

The numbers are pairs of ions/c.c./sec. in air of 1 atm. pressure.
The numbers within parentheses are numbers of records. N = North, S = South.

As is seen in Table 2, the ionisation in 1932–33 *decreased* during auroræ and also with their extension to the southern horizon and with the intensity of the auroræ (scale: 0–4). It is curious that this decrease, expressed as a percentage of the ionisation with a clear sky and no aurora, is greatest when the vessel was shielded from above by a lead shield of 10 cm. thickness, that is, for the harder radiation.

V. F. Hess and R. Steinmaurer[4] have found mainly a decrease of the ionisation during magnetic storms in the period September 1931–March 1933 from their records at Hafelekar, near Innsbruck. Like the results from the second period at Abisko (great auroral displays being always accompanied by magnetic disturbances, which probably cause the change of the ionisation) this is in "apparent contradiction" to the results from the first period at Abisko. Studying Table 4 of the exhaustive paper by R. Steinmaurer and H. Graziadei[5], we find that in 1931 there were 4 increases and 1 decrease during 5 magnetic storms, but in 1932 there were 3 increases and 15 decreases during 18 magnetic storms. Thus the material from Hafelekar indicates a change from mainly increasing to mainly decreasing ionisation during magnetic storms in 1931–32.

At the present time, I cannot see any other explanation of the above mentioned "apparent contradiction" between 1929–30 and 1932–33 than that some connexion exists between the ionisation and the sunspot period. The last sunspot maximum occurred at 1928·4, and the relative numbers for 1929 and 1930 were 65·0 and 35·7 respectively. For 1932 the relative number was 11·1, and the sunspot minimum occurred in 1933.

The mechanism of the relation of terrestrial magnetism to cosmic ultra-radiation is still unknown, but as we now know no cause why the ultra-radiation should behave in opposite ways during magnetic storms at sunspot maxima and sunspot minima, it seems to me more probable that the cosmic ultra-radiation always decreases during magnetic storms, and that the observed increase of the ionisation in 1929–30 is caused by an increased influence from the sun at sunspot maxima. This influence may be either an increased penetrating radiation from the sun itself, capable of reaching sea-level, or, possibly, an increased secondary radiation of the cosmic ultra-radiation, caused directly or indirectly by the solar corpuscles, which to some extent produce the auroræ.

Certain phenomena observed by other investigators[6] seem to support this explanation. Also the minor decrease of the ionisation for the open shield during magnetic storms at Abisko in 1932–33, mentioned above, may be due to a remaining primary or secondary soft radiation from the sun, tending to increase the ionisation.

AXEL CORLIN.

Observatory,
Lund.
Nov. 17.

---

[1] Cf. *Phys. Z.*, **31**, 1065; 1930; and *Lund Obs. Circ.*, 1 and 6, 1931–32.

[2] *Lund Obs. Circ.*, 1, 1931.

[3] *Medd. Lund Obs.*, **2**, No. 67; 1934.

[4] NATURE, **132**, 601, Oct. 14, 1933.

[5] *Berlin Ber.*, **22**; 1933.

[6] V. F. Hess, NATURE, **127**, 10, Jan. 3, 1931; and *Z. Phys.*, **71**, 171; 1931. O. Freytag, *Gerl. Beitr.*, **39**, 1; 1933. E. Regener, NATURE, **132**, 696, Nov. 4, 1933.

Electrolytic Concentration of Diplogen

WE have recently made some preliminary investigations of the effect of various factors on the efficiency of the concentration of diplogen by electrolysis in alkaline solution. The diplogen-hydrogen ratio at various stages was determined by specific gravity measurements after repeated distillation. These measurements were carried out in pyknometers of 5 c.c. and 25 c.c. capacity with an estimated accuracy of one part in a hundred thousand. In calculating the diplogen concentrations, we have used Lewis's[1] value for the specific gravity of pure D_2O and Bleakney and Gould's[2] estimate of the D/H ratio in ordinary water.

We have investigated the influence of the following factors: (*a*) the nature of the cathode metal, (*b*) the concentration of the electrolyte, (*c*) the temperature of the electrolyte, and (*d*) the current density at the cathode. We have expressed the efficiency of the separation by the factor α, defined by Lewis and Macdonald[3] by means of the equation

$$d \ln \mathrm{D} = \alpha \, d \ln \mathrm{H} \qquad (1)$$

A correction was made for evaporation and the maximum error in our values of α is estimated to be ± 0·05. The following results were obtained :

Effect of Cathode Metal

Stage of concentration : D/H = 0·1–0·3 per cent

Cathode	Electrolyte	α
Ni	1 per cent NaOH	0·22
Pt	,,	0·19
Cu	,,	0·19

Effect of Concentration of Electrolyte

Stage of concentration : D/H = 0·1–0·3 per cent

Cathode	Electrolyte	α
Ni	1 per cent NaOH	0·22
Ni	8 per cent NaOH	0·20

Effect of Temperature

Stage of concentration : D/H = 0·25–0·5 per cent

Cathode	Electrolyte	Temperature	α
Ni	2 per cent NaOH	10° C.	0·23
Ni	2 per cent NaOH	100° C.	0·26

Effect of Current Density

Stage of concentration : D/H = 0·05–0·15 per cent

Cathode	Electrolyte	Current Density	α
Ni	1 per cent NaOH	10 amp./cm.^{2}	0·18
Ni	1 per cent NaOH	0·07 ,,	0·27

The most striking feature of these results is that the factor α is unexpectedly insensitive to the conditions of electrolysis. Neither the temperature nor the nature of the cathode metal appears to have any effect on the efficiency of separation, and it is doubtful whether the small difference observed in the current density experiments is greater than the experimental error.

It may appear strange that the efficiency is not affected by the differences in hydrogen over-voltage of the metals employed. Such a state of affairs is, however, in accordance with the theory of over-voltage advanced by Gurney[4]. He derives the following expression for the rate of discharge of hydrogen ions at an inert electrode :

$$\ln i_{\mathrm{H}} = \frac{E_0 - E_1 + \varepsilon V}{\gamma k T} + \log T + \text{constant} \qquad (2)$$

where i_{H} is the current density, E_0 is the neutralisation energy of an H_3O^+ ion in its lowest energy state by an electron, E_1 is the work function of the metal, ε is the electronic charge and V is the applied cathodic potential ; γ is a correction factor a little greater than unity. The discharge of diplogen from the ion DH_2O^+ at the same cathode is governed by an exactly similar expression except that the value of E_0 will be different in the two cases. The nature of the cathode should therefore have no effect on the ratio $i_{\mathrm{D}}/i_{\mathrm{H}}$, in agreement with our results.

The actual value of $i_{\mathrm{D}}/i_{\mathrm{H}}$ $(= \alpha)$ is given by the relation

$$\ln \alpha = \ln \frac{i_{\mathrm{D}}}{i_{\mathrm{H}}} = \frac{(E_0)_{\mathrm{D}} - (E_0)_{\mathrm{H}}}{\gamma k T} \qquad (3)$$

The difference in the E_0 values in the two cases depends on the difference in zero point energy of the two links O—H and O—D, which has been calculated by Sherman and Eyring[5] as 1,400 calories per mole. The insertion of this value in equation (3) leads to our observed separation coefficient (which agrees with that found by Lewis[3]), if γ is given the plausible value of 1·4. It may be noted that on the basis of equation (3) the influence of temperature on α over the temperature range studied is just within our present experimental error, but could be observed with a slight increase in accuracy.

The above results are provisional, and more accurate investigations are in progress.

R. P. BELL.
J. H. WOLFENDEN.

Physical Chemistry Laboratory,
Balliol College and Trinity College,
Oxford.

---

[1] G. N. Lewis and R. T. Macdonald, *J. Amer. Chem. Soc.*, **55**, 3057; 1933.

[2] W. Bleakney and A. J. Gould, *Phys. Rev.*, **44**, 265 ; 1933.

[3] G. N. Lewis and R. T. Macdonald, *J. Chem. Phys.*, **1**, 341 ; 1933.

[4] R. W. Gurney, *Proc. Roy. Soc.*, A, **134**, 137 ; 1931.

[5] A. Sherman and H. Eyring, *J. Chem. Phys.*, **1**, 345 ; 1933.

Catalytic Hydrogen Replacement and the Nature of Over-voltage

IN NATURE of December 16, 1933, J. Horiuti and M. Polanyi state that they have found that the replacement of heavy hydrogen in water under the catalytic influence of platinum black is faster in pure water than in either acid or alkaline solutions, and suggest that these observations "seem to settle the question" of the nature of the inertia which is responsible for the hydrogen over-voltage at platinum electrodes. There are, however, a number of other possibilities besides the two mentioned by Horiuti and Polanyi. I need only mention one, namely, that the effect of the acids and bases may be merely to cause a partial coagulation of the particles of the platinum, thus reducing the area available for the catalysis. Until such possibilities have been excluded, no definite conclusions as to the mechanism of the process can legitimately be drawn and it certainly appears to be extravagant to suggest that the experiments settle the question of the hydrogen over-voltage.

J. A. V. BUTLER.

University of Edinburgh.

Reaction Rates of the Hydrogen Isotopes

IT seems to be generally assumed that diplogen will always react more slowly than hydrogen. As I may partly be responsible for this view[1], I should like to point out that this is not always correct. Lower reactivity of diplogen compared with hydrogen results mainly from two causes : (1) the existence of zero point energy ; and (2) the quantum mechanical leakage of particles through energy barriers. Whilst the leakage through the barrier is always greater for the hydrogen than for the diplogen atoms, the effect of the zero point energy may occasionally favour the reverse ratio. I will confine myself to one special case, as the general treatment will be published shortly by C. E. H. Bawn and G. Ogden. Compare the reaction of a free hydrogen and a diplogen atom ; in the initial state the atoms possess no zero point energy and their energies will be equal. However, at the top of the barrier there will be a zero point energy present[2], and this will be greater for the complex reacting with the hydrogen