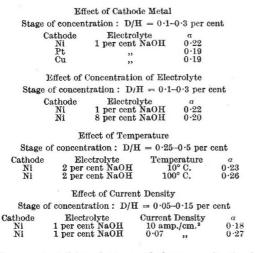of the electrolyte, and (d) the current density at the cathode. We have expressed the efficiency of the separation by the factor α, defined by Lewis and Macdonald[3] by means of the equation

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

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 :

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

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_D/i_H, in agreement with our results. The actual value of i_D/i_H ($= \alpha$) is given by the relation

$$\ln \alpha = \ln \frac{i_D}{i_H} = \frac{(E_0)_D - (E_0)_H}{\gamma k T} \qquad (3)$$

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.

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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.

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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