

### 293. *Adsorption at the Surface of Solutions. Part I. The Surface Composition of Water-Alcohol Solutions.*

By J. A. V. BUTLER and A. WIGHTMAN.

IN his treatment of the thermodynamics of capillarity, Gibbs ("Scientific Papers," I, p. 33) considered the matter enclosed between two surfaces, drawn one on each side of the interface and placed so that the matter is perfectly homogeneous outside them on each side. If a dividing surface, drawn sensibly parallel with the physical discontinuity, is now placed within this region, the surface excess of each component may be defined as the difference between the actual amount present between two surfaces and the amount which would be present if each phase continued to be perfectly homogeneous up to the dividing surface. If  $\Gamma_1, \Gamma_2$ , etc., are the surface excesses of the components A, B, etc., for unit area of the surface, Gibbs obtained the equation

$$\Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 + \dots + d\sigma = 0,$$

where  $\sigma$  is the surface tension and  $\mu_1, \mu_2$ , etc., the chemical potentials of the components. In the case of a binary solution the dividing surface may be so placed that  $\Gamma_1 = 0$ ; the surface excess of B is then given by  $\Gamma_2 = -d\sigma/d\mu_2$ .

The first exact application of this equation to concentrated binary solutions, giving  $d\mu_2$  its precise value  $RT \cdot d \log p_2$ , was made by Schofield and Rideal (*Proc. Roy. Soc.*, 1925, A, 109, 57). They found that in the case of water-ethyl alcohol solutions, the adsorption had a maximum value of about  $41 \times 10^{13}$  mols./cm.<sup>2</sup> for solutions containing about 25 mols. % of alcohol, and fell sharply as the alcohol content increased, reaching values between  $17$  and  $14 \times 10^{13}$  between 60 and 100 mols. %. They suggested as possible explanations of the maximum, (1) that the orientation of the alcohol molecules changes considerably in the more concentrated solutions, (2) that at the higher concentrations water is adsorbed under a nearly complete surface layer of alcohol.

Wynne Jones has recently pointed out (*Phil. Mag.*, 1931, 12, 907) that since the Gibbs equation determines the surface excess of the solute, in order to obtain the true amount present at the surface it is necessary to add to the calculated adsorption a quantity depending on the concentration in the solution. The vapour pressures employed by Schofield and Rideal for evaluating the adsorptions were rather inaccurate. Using the more recent vapour pressure measurements of Dobson (*J.*, 1925, 127, 2866), Wynne Jones obtained an adsorption

curve which had a maximum at about 10 mols. % of alcohol and, when plotted against the weight fraction of alcohol, fell almost linearly as the concentration increased. He postulated that the amount to be added to the Gibbs adsorption in order to obtain the actual amount present at the interface was proportional to the concentration. The proportionality factor was taken as the slope of the linear part of the curve, which on this view is due to a complete surface layer of alcohol molecules, each occupying  $20.3 \text{ \AA}^2$ . Harkins and Wampler (*J. Amer. Chem. Soc.*, 1931, **53**, 850) have also given a term to be added to the Gibbs adsorption in concentrated solutions. One of us has recently pointed out (Butler, *Proc. Roy. Soc.*, 1932, *A*, **135**, 348, footnote) that this estimate is excessive, for in the case of a surface layer containing  $v_1$  molecules of A, and  $v_2$  molecules of B, the number of molecules of B which would accompany  $v_1$  molecules of A if present in the surface in the same proportion as in the bulk of the solution is  $v_2.N_2/N_1$ , where  $N_1$ ,  $N_2$  are the molar fractions of A and B in the solution, so that the relation between the surface excess and the actual number of molecules present in the surface is  $\Gamma_2 = v_2 - v_1.N_2/N_1$ .

The values of  $\Gamma$  calculated by the Gibbs equation are seriously affected by even small errors in the surface tensions and in the partial vapour pressures, and it would not be profitable to discuss in detail the form of the adsorption curve unless very reliable values of these quantities were available. The partial vapour pressures of ethyl alcohol-water solutions at  $25^\circ$  have been investigated by Dobson (*loc. cit.*) and by Shaw and Butler (*Proc. Roy. Soc.*, 1930, *A*, **129**, 519). The results of the two investigations are in good agreement and between them provide a considerable number of values spread over the whole range from 0 to 100% of alcohol. The most extensive series of determinations of the surface tensions of these solutions is that of Bircumshaw (*J.*, 1922, **121**, 877), obtained by the drop-weight method. Since all measurements of surface tension are indirect, it seemed very desirable to confirm these by another method, and for this purpose we have made use of the maximum bubble pressure method as developed by Sugden (*J.*, 1922, **121**, 858; 1924, **125**, 27).

#### EXPERIMENTAL.

The EtOH was prepared by Butler and Robertson's method (*Proc. Roy. Soc.*, 1929, **125**, 694). Solutions were made by weighing the requisite amounts of  $\text{H}_2\text{O}$  and EtOH in a stoppered flask. The apparatus (compare Mills and Robinson, *J.*, 1931, 1629) consisted of a bulb fitted with two ground-in tubes carrying the fine and coarse jets, which were adjusted so that their tips were at the same level. The larger jet was 0.2 cm. in radius, and the other a very narrow capillary giving a max. bubble pressure in  $\text{H}_2\text{O}$  of about 40 cm. of  $\text{H}_2\text{O}$ .

The vessel was connected with a H<sub>2</sub>O manometer and an arrangement for gradually reducing the pressure. In practice, one of the tubes was plugged at the top, and the pressure was gradually lowered until air bubbles began to emerge from the other jet. The tap connecting with the pressure-reducing apparatus was then closed, and when the bubbles ceased the pressure difference was read on the manometer. The air was dried by passing through a CaCl<sub>2</sub> tower before entering the tubes. The bulb and the manometer were almost completely immersed in the H<sub>2</sub>O of a glass-sided thermostat, electrically maintained at 25° ± 0.02°. The pressure difference was read by means of an accurate cathetometer, reading to 0.005 cm. Provided that the whole apparatus were kept scrupulously clean, and the capillary free from obstruction, and when the pressure in A was only allowed to fall a little below that required to produce bubbles, reproducible results were obtained without difficulty. Measurements were made with at least two samples of each solution. In a few cases concordant readings were not at first obtained. The capillary was then cleaned, and the measurements repeated until several concordant series had been obtained. The following readings, made with 80% EtOH, are given as an example of the experimental figures.

Sample I. Coarse jet : 1.75, 1.74, 1.75, 1.74, 1.74, 1.74 cm.

Fine jet : 13.12, 13.12, 13.13, 13.12, 13.13, 13.15 cm.

Sample II. Coarse jet : 1.73, 1.73, 1.73 cm.

Fine jet : 13.12, 13.11, 13.12, 13.12 cm.

Mean jet pressure difference of solution, 11.39 cm.

The surface tensions were calc. by Sugden's formula,  $\sigma = AP_1(1 + 0.69r_2D/P_1d_0)$ , where  $P_1$  is the mean jet pressure diff. in cm. of water,  $r_2$  the radius of the coarse jet,  $D$  the density of the solution and  $d_0$  that of H<sub>2</sub>O;  $A$  is a const. which depends on the radius of the fine jet. This was not measured directly, but  $A$  was determined by determining  $P_1$  for H<sub>2</sub>O, for which the surface tension was taken as 71.97 dynes/cm. at 25° (International Critical Tables). For the two capillaries employed,  $A$  had the values 2.0251 and 1.8240. The densities employed in evaluating the term  $0.69r_2D/P_1d_0$  need not be known with great accuracy : those values used were taken from International Critical Tables (Vol. III, p. 116).

TABLE I.

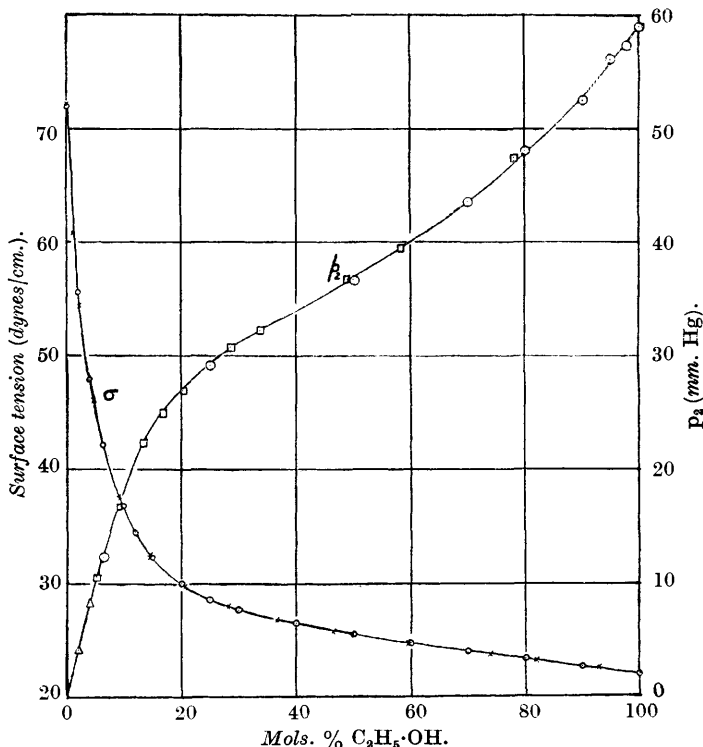
Mols. % EtOH.	$P_1$ , cm.	$P_2$ , cm.	$D$ .	$\sigma$ .	Mols. % EtOH.	$P_1$ , cm.	$P_2$ , cm.	$D$ .	$\sigma$ .
100	10.72	—	0.7850	21.93	20	—	16.30	0.9335	29.97
90	11.04	—	0.7975	22.59	15	—	17.52	0.9448	32.20
80	11.39	—	0.8109	23.29	12	—	18.74	0.9575	34.42
70	11.70	—	0.8250	23.93	10	—	20.03	0.9633	36.79
60	12.06	—	0.8409	24.67	6.4	20.67	—	0.9735	42.13
50	—	13.82	0.8589	25.43	4	—	26.10	0.9810	47.86
40	12.92	—	0.8823	26.41	2	—	30.33	0.9880	55.57
40	—	14.38	0.8823	26.45	0	35.40	—	0.9971	71.97
30	—	15.01	0.9047	27.60	0	—	39.32	0.9971	71.97
25	13.94	—	0.9186	28.49					

Table I gives the experimental data and the calc. surface tensions. The max. value of the correction made by the term  $(0.69r_2D/P_1d_0)$  is 0.14 dyne in 100% EtOH. The surface tensions together with Bircumshaw's values are plotted against the molar fraction of alcohol in Fig. 1. There is no serious discrepancy between the two sets of values. Bircumshaw's values for H<sub>2</sub>O

and EtOH (both measured directly) are somewhat higher than the I.C.T. value for  $H_2O$ , which we have taken as standard, and the value for EtOH obtained therefrom by us. The recalculation of Bircumshaw's values, making his value for  $H_2O$  coincide with ours, would not, however, improve the agreement of the intermediate values. Our values are more concordant among themselves than his, and when plotted on a large scale only two points fall appreciably away from a smooth curve: these are for 80% and 10% EtOH,

FIG. 1.

*Surface tensions and partial vapour pressures of ethyl-alcoholic solutions.*



Surface tension:  $\times$  Bircumshaw.  $\odot$  this paper. Partial vapour pressures:  $\square$  Dobson.  $\odot$  Shaw and Butler.  $\triangle$  Thomson (unpublished).

the smoothed surface tensions of which are 23.26 instead of 23.29, and 36.72 instead of 36.79. The experimental error, assuming that the theoretical basis is correct, may be estimated as well within  $\pm 0.05$  dyne.

In connexion with the measurements to be described in Part II (following paper), the surface tensions of some of these solutions have been determined by the capillary-rise method, the proper corrections being made (Sugden, J., 1921, 119, 1483): the values obtained by the two methods are compared below:

*Surface tensions of aqueous ethyl-alcoholic solutions at 25°.*

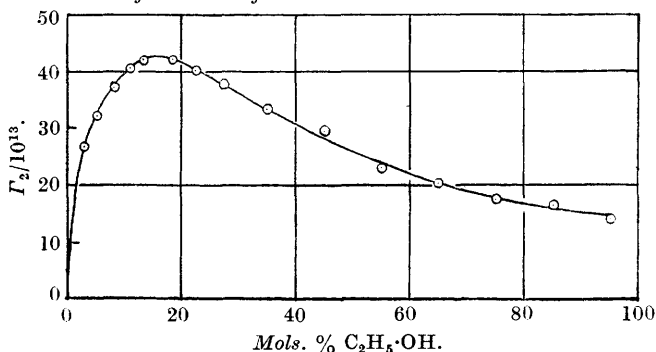
Mols. % EtOH	.....	80.0	50.0	25.0	6.4	2.0
$\sigma$ (capill. rise)	.....	23.28	25.53	28.55	42.19	55.49
$\sigma$ (max. bubble press.)	.....	23.29	25.43	28.49	42.13	55.57

Although the capillary-rise determinations probably do not represent the highest accuracy attainable by this method, they are in reasonable agreement with the other values. It is thus demonstrated that the surface tensions of ethyl-alcoholic solutions determined by three methods, when the proper corrections are applied, are in substantial agreement with each other.

TABLE II.

Mols. % EtOH.	$\sigma$ .	$\log p_2$ .	$\Gamma_2 \times 10^{-13}$ .	Mols. % EtOH.	$\sigma$ .	$\log p_2$ .	$\Gamma_2 \times 10^{-13}$ .
100	21.93	1.771	—	25	28.49	1.467	37.8
90	22.59	1.722	14.0	20	29.97	1.428	40.3
80	23.26	1.679	16.5	15	32.20	1.372	42.3
70	23.93	1.639	17.5	12	34.42	1.316	42.2
60	24.67	1.600	20.4	10	36.72	1.256	40.7
50	25.43	1.565	23.0	6.4	42.13	1.097	37.2
40	26.43	1.529	29.5	4	47.86	0.908	32.2
30	27.60	1.492	33.5	2	55.57	0.602	26.8

FIG. 2.

*Surface excess of alcohol in water-alcohol solutions.*


In order to calculate the Gibbs adsorptions, the partial v.p.'s of EtOH of the solutions were obtained by graphical interpolation from the combined results of Dobson and of Shaw and Butler. In practice, it was found easier to interpolate for the higher percentages of alcohol from the  $\log p-N$  curve. Table II gives (1) the smoothed values of the surface tensions, (2) the values of  $\log p_2$ , and (3) the mean adsorptions for the intervals between one given solution and the next, as given by  $\Gamma_2 = 1.062 \times 10^{13} (-\Delta\sigma/\Delta \log_{10} p)$  mols. per cm.<sup>2</sup>. The const. in this equation is the value of  $2.303kT$  at 25°, where  $k$ , the gas const. per mol., is taken as  $1.372 \times 10^{16}$  ergs. The values of  $\Gamma_2$  plotted against the mean molar fraction for the interval to which they apply are shown in Fig. 2.

*Discussion.*

The relation between the actual amount of a substance present near the interface and the Gibbs adsorption can be obtained by a

small modification of Gibbs's derivation. Suppose that two surfaces, containing the whole of the non-homogeneous interfacial region, have between them  $n_1$  molecules of  $S_1$  and  $n_2$  molecules of  $S_2$ , per sq. cm. of interface. It can easily be shown by the method used by Gibbs that

$$n_1 d\mu_1 + n_2 d\mu_2 + d\sigma = 0. \quad (1)$$

where  $\mu_1, \mu_2$  are the chemical potentials per mol. If  $N_1, N_2$  are the molar fractions in the bulk of the solution,  $d\mu_1$  and  $d\mu_2$  are related at constant temperature and pressure by the equation  $N_1 d\mu_1 + N_2 d\mu_2 = 0$ , so that (1) may be written as

$$(n_2 - n_1 \cdot N_2/N_1) d\mu_2 + d\sigma = 0 \quad (2)$$

Since the Gibbs adsorption is  $\Gamma_2 = -d\sigma/d\mu_2$ , we thus have

$$\Gamma_2 = n_2 - n_1 \cdot N_2/N_1 \quad (3)$$

We can thus find  $n_2$ , *i.e.*, the actual amount of  $S_2$  present within any given distance of the surface, if we know  $n_1$ . There is one case in which this equation can be simplified, *viz.*, when the discontinuity only affects a single surface layer of molecules. Then if  $v_1, v_2$  are the numbers of molecules of  $S_1$  and  $S_2$  per sq. cm. in the surface layer, and  $A_1, A_2$  their superficial areas, we have

$$A_1 v_1 + A_2 v_2 = 1 \quad (4)$$

If the two surfaces are now drawn so that they contain between them only the surface layer as defined by (4), (3) becomes

$$\Gamma_2 = v_2 - v_1 \cdot N_2/N_1 \quad (5)$$

or, introducing the value of  $v_2$  given by (4),

$$\Gamma_2 = 1/A_2 - (A_1/A_2 + N_2/N_1)v_1 \quad (6)$$

It is thus possible in this case to determine the actual composition of the surface layer from  $\Gamma_2$  if  $A_1$  and  $A_2$  are known.  $1/A_2$ , which is the maximum number of molecules of  $S_2$  which can be present in unit area, may be denoted by  $v_2^0$ .

Let the experimentally determined values of  $\Gamma_2$  be plotted against the molar ratio  $N_2/N_1$  of the solution, giving the curve CE (Fig. 3). Let the point P have the co-ordinates  $v_2^0, -A_1/A_2$ . If D is any point on the curve CE, it is evident from (5) that the slope of the line PD is equal to the value of  $v_1$  for the point D. Also the value of  $v_2$  is given by the intercept of the line PD on the axis OY.

Now, if we do not know the values of  $v_2^0$  and  $-A_1/A_2$  from other sources, we have only this consideration to guide us in choosing the position of P. It is probable that, as the water content of the solution decreases, the number of water molecules in the surface also continuously decreases. If this is so the point P must be so

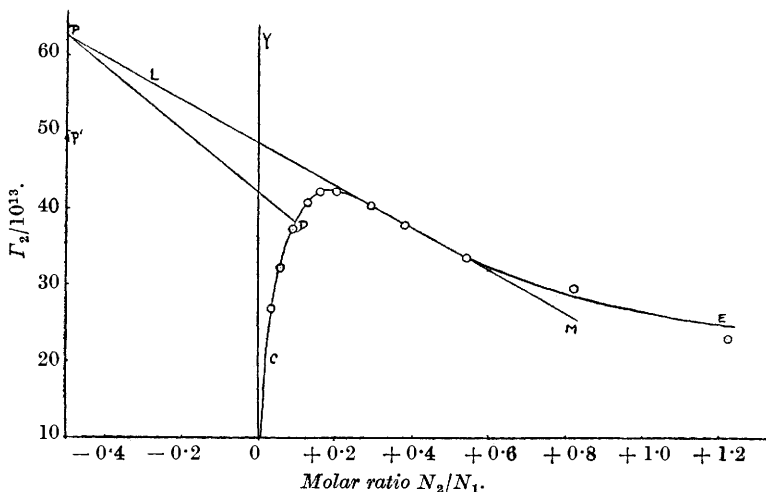
placed that the slopes of the lines like PD decrease continuously as  $N_2/N_1$  increases.

It will be observed that the experimental points are almost linear for values of  $N_2/N_1$  between 0.2 and 0.5. Drawing the line LM through these points, it is evident that the requirement stated above can only be satisfied if the point P is placed on or above this line. Suppose that the point P lies on the line LM. For every value of  $v_2^0$  there will now be a corresponding value of  $A_1/A_2$ . It follows that

if  $A_1/A_2 = 0.5$ ,  $v_2^0 = 62.5 \times 10^{13}$  and  $v_1^0 = 125 \times 10^{13}$ ;

if  $A_1/A_2 = 1.0$ ,  $v_2^0 = 76.5 \times 10^{13}$  and  $v_1^0 = 76.5 \times 10^{13}$ .

FIG. 3.



If the point P lies above the line LM the corresponding values of  $v_2^0$ ,  $v_1^0$  will be greater.\*

According to Adam, the area per molecule of closely packed hydrocarbon chains in insoluble films is  $20.5 \text{ \AA}^2$ , corresponding to  $48.8 \times 10^{13}$  mols./cm.<sup>2</sup>. It is evident that if the number of water molecules in the surface layer decreases continuously as the water content of the solution decreases, then (a) if  $v_2^0$  corresponds with the value for close packed hydrocarbon chains in insoluble films, the area of the water molecule must be only about 0.1 of the area of the alcohol molecule, (b) if the ratio of the area of the water molecule to that of the alcohol molecule is greater than 0.5, the value of  $v_2^0$

\* It is not necessary to assume that  $A_1$ ,  $A_2$  are constant for the whole range of solutions. If they are variable, the position of P will vary; the arguments given would not be invalidated by such variation.

must be greater than  $62.5 \times 10^{13}$ . Since neither of these consequences is acceptable, we are faced with the following alternatives :

(I) If the adsorption is limited to a surface layer characterised by (4),  $\nu_1$  increases and therefore  $\nu_2$  decreases as the water content of the solution is decreased in solutions containing between 20 and 30 mols. % of alcohol.

(II) The adsorption layer is not truly unimolecular, and equation (4) is not sufficient to characterise the whole of the matter affected by the vicinity of the interface.

If we still regard (I) as improbable, we are obliged to accept (II) as being most in accordance with the facts.

The difference between the observed values of the adsorption and those which would be consistent with a surface layer characterised by (4) is, however, comparatively small. The form of the adsorption curve can be accounted for if it be supposed that there is a small excess of alcohol molecules just below the surface layer in certain solutions. It will be of interest to make an estimate of the amount of adsorption below the surface layer which would have to be assumed in order to avoid conflicting with the condition stated above. We shall assume that  $\nu_2^0 = 49 \times 10^{13}$ , corresponding to the minimum area of hydrocarbon chains in insoluble films, and that  $A_1/A_2 = 0.5$ , or  $\nu_1^0 = 98 \times 10^{13}$ , which is in reasonable agreement with the dimensions of the water molecule. The figures given in Table III, which have been deduced by a graphical method based on Fig. 3, the point P for these quantities taking the position P', correspond to the minimum adsorption below the surface layer, which satisfies the conditions, for these molecular dimensions.  $\nu_2$  and  $\nu_1$  are the numbers of molecules of alcohol and water in the surface layer,  $\Gamma_2'$  the excess of alcohol in the surface layer as given by (5),  $\Gamma_2''$  the excess of alcohol below the surface layer, and  $\Gamma_2$ , the sum of  $\Gamma_2'$  and  $\Gamma_2''$ , agrees with the Gibbs adsorption. If greater values were taken for the adsorption below the surface layer it would be possible to find lower values of  $\nu_2$  which would also be consistent with the observed adsorptions; but the figures given may be regarded as a reasonable estimate of the surface composition.

TABLE III.

*Estimated composition of the surface of water-alcohol solutions (molecules/cm.<sup>2</sup>  $\times 10^{13}$ ).*

$N_2$ .	$\nu_2$ .	$\nu_1$ .	$\Gamma_2'$ .	$\Gamma_2''$ .	$\Gamma_2$ .	$N_2$ .	$\nu_2$ .	$\nu_1$ .	$\Gamma_2'$ .	$\Gamma_2''$ .	$\Gamma_2$ .
0	0	98	0	0	0	27.5	41	16	35	3	38
3	28	42	27	0	27	35	41	16	32	1	33
8.2	38	22	36	1	37	55	42	15	23	0	23
11	39	20	36.5	4.5	41	75	44.5	9	17	0	17
13.5	40	18	37	5	42	95	48	1.8	14	0	14
22.5	41	16	36	4	40	100	49	0	—	—	—



Schofield and Rideal (*Phil. Mag.*, 1932, **13**, 806) have reasserted their original view (*loc. cit.*) that the fall in the surface excess in concentrated alcoholic solutions is due to the formation of a layer relatively rich in water below a closely packed surface layer of alcohol. Their conclusion depends on the assumption that a complete surface layer of alcohol exists at the surface, and they overlook the fact that a small proportion of water molecules in the surface layer reduces the surface excess in the more concentrated solutions by a much greater extent than the area they occupy.

*Summary.*

1. The surface tensions of aqueous ethyl-alcoholic solutions have been determined at 25° by the maximum bubble pressure method. The values obtained are in agreement with those of Bircumshaw, made by the drop-weight method, and with some determinations made by the capillary-rise method. The values of the Gibbs adsorption have been calculated.

2. A relation has been given between the Gibbs adsorption and the total number of molecules present at the surface.

3. It is shown that the observed adsorptions are inconsistent with the hypothesis that only a single layer of molecules at the surface differs in composition from the bulk of the solution. The difference between the requirements of this hypothesis and the observed adsorptions is, however, comparatively small.

One of us (A. W.) is indebted to the Department of Industrial and Scientific Research for a maintenance grant.

THE UNIVERSITY, EDINBURGH.

[Received, June 9th, 1932.]

---