EFFECTS OF AN ELECTROLYTE ON THE
ACTIVITIES OF WATER AND ALCOHOL
IN MIXTURES.

by

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INTRODUCTION.

In the interaction between ions and solvent
molecules, two types of physical effects have been
recognised. The first may be called the solvation
effect, and, in the absence of chemical compound
formation between ions and solvent, this may be
ascribed to the attraction exerted by the electric
field of the ions on the polarisable molecules of
the solvent. Since an element of dielectric with a
dielectric constant greater than one tends to move
into regions where the electric field is greatest,
molecules of water, a substance with a high dielect-
ric constant, will tend to congregate round the ions
and will be held by quite considerable forces. The
attraction of water molecules will result in the
squeezing out of other ions from the vicinity of a
given ion, and hence the distribution of ions under
the influence of the field of the central ion, and
that of the "ion atmosphere" according to the Debye-
Hückel calculation (Physik. Z., $\underline{25}$ 97, 1924) will be
disturbed. It has been shown by Butler (J. Phys.
Chem. $\underline{33}$, 1015, 1929) that this effect may be of
primary importance in determining B in the equation

$$\log f = \frac{- A \sqrt{\mu}}{1 + C \sqrt{\mu}} + B\mu ,$$

the /

the linear term of which was introduced by Hückel from a consideration of the lowering of the dielectric constant of water produced by the addition of an electrolyte (Physik. Z. $\underline{26}$, 93, 1925).

When a non-electrolyte C is added to an aqueous solution of an electrolyte, the second effect, usually known as the salting-out effect, may be observed. If this substance is less polarisable than water, water molecules will be attracted by the ions more strongly than the molecules of C, and the latter will thus be salted-out from the vicinity of the ions. As a result of this, the apparent concentration of C is increased in the bulk of the solution.

This effect has been studied almost exclusively in dilute aqueous solutions, either by means of solubility measurements with sparingly soluble non — electrolytes, or by distribution measurements, between the aqueous solution and an immiscible solvent in which the electrolyte is not soluble.

In a saturated solution of C, the activity is necessarily constant. If C is sparingly soluble, then we may write,

$$S_0 = \alpha_0$$

Where S_0 is the solubility of C in water, and

α_0 is the activity of C in aqueous solution. If f is the activity coefficient of C in any solution and S is its solubility, then,

$$f s = \alpha$$

where/

where α is the activity of C in the solution.

But the activity is constant and equal to α_0.

Hence $\qquad f s = \alpha_0$

$$f = \frac{\alpha_0}{S}$$

or $\qquad f = \frac{So}{S}$ $\qquad$ ----------- (1)

Setschenow (Ann. Chim. Phys. <u>25</u> 226, 1892)
studied the solubilities of various gases in aqueous
and salt solutions. He found that the solubility
of a gas was lowered by increasing concentrations of
salt, and expressed his results by the empirical
formula,

$$\ln\left(\frac{So}{S}\right) = kc \qquad \text{----------} \qquad (2)$$

where So $\ =$ solubility of the gas in water

$\quad\quad\quad$ S $\ =$ solubility in salt solution

$\quad\quad\quad$ C $\ =$ concentration of salt in moles per litre

$\quad\quad\quad$ k $\ =$ a constant for a given salt.

From equation (1) this may be written as

$$\log f = k c \qquad \text{-----------------} \qquad (2a)$$

Rothmund (Z. Phys. Chem. <u>33</u> 401, 1900) has shown that
the solubility of phenylthiocarbamide is smaller in
salt solutions than it is in water, the decrease
depending on the concentration of salt. Different
salts were found to depress the solubility to
different degrees, and an anomalous result was given
with/

with ammonium nitrate, which increased the solubility.
Rothmund found that in general his results satisfied
the requirements of the empirical equation,

$$\frac{S_0 - S}{S_0} = k c \quad \text{---------------} \quad (3)$$

where the symbols have the same significance as in
equation (2)

This equation may be written in the form

$$1 - \frac{S}{S_0} = k c$$

which, using the relationship in (1), becomes

$$\frac{1}{f} = 1 - k c \quad \text{-----------------} \quad (3a).$$

Glasstone and Pound (J.C.S., 127, 2660, 1925)
carried out experiments on the solubility of ethyl
acetate in aqueous solutions of the alkali halides,
and also of certain non-electrolytes. They found that
the addition of such substances lowered the solubility
of ethyl acetate, the only exceptions being found
where the added substance (salt or nonelectrolyte)
was soluble in ethyl acetate. From the solubility
lowerings produced by electrolytes, they calculated
hydration values for the cations on the assumption
that the lowering of the solubility was due to the
removal of water molecules by these ions to form
hydrates, with the result that these water molecules
became fixed, and were no longer solvent molecules
for the ethyl acetate. As they could not, however,
obtain/

obtain an equation to fit all the cases, and since
non-electrolytes also reduced the solubility they
pointed out that this could not be the only influence
in operation.

In a later paper, Glasstone, Dimond, and Jones,
(J.C.S. 129 2935, 1926), attempted an explanation of
the phenomenon on the grounds that the addition of a
salt to water increases its already large internal
pressure and hence reduces still further its solvent
power for a non-polar substance.   Sugden (J.C.S. 129,
174, 1926) suggested that while cations produce this
salting-out effect, by attracting solvent molecules
into their vicinity, anions have varying depolymerising
effects on the water, thus producing an opposing
effect.   This would explain the increase in solubility
in some cases.

A mathematical theory of the distribution of two
kinds of molecules round an ion has been worked out
by Debye and McAulay (Physik. Z. 26 22, 1925).
They find that the deviation of the activity coeff-
icient of the non-electrolyte from unity, due to the
effect of the non-electrolyte in reducing the di-
electric constant of water, is given to a first
approximation by the equation,

$$\ln f_2 = \alpha n' \frac{\sum \nu_i z_i^2 e^2}{2 D^\circ r . k . T .} \quad ,$$

where f_2 is the activity coefficient of the non-
electrolyte, n^1 is the no. of molecules of salt per
c.c. of solution, ν_i is the no. of ions of the
i^{th} kind, e is the electronic charge, D^o is the
dielectric constant of water, r is the mean ionic
radius, k is the Boltzmann constant, and T is the
absolute temperature. The constant, α, is defined
by the relation $D = D^o (1 - \alpha n)$, where D is the
dielectric constant of the solution containing n
molecules of the non-electrolyte per c.c.

From a collection, and study, of all the avail-
able data dealing with the activity coefficients of
gases, sparingly soluble non-electrolytes, and the
undissociated parts of weak electrolytes in salt
solutions, Randall and Failey (Chem. Reviews 4, 271,
1927) have shown that there is a qualitative agreement
with this equation.

The object of the present investigation was to
determine the effect of an electrolyte on a mixed
solvent where the proportion of each constituent could
be varied from 0 to 100%. It was hoped that such
an investigation would give information as to the
relative importance of the solvation and the salting-
out effects over the whole range of compositions.

The system water-alcohol was chosen, with
lithium chloride, one of the few salts which are
soluble to a considerable extent in both components,
as/

as the electrolyte. The only method by which the
activities of water and alcohol can be determined is
by measuring their partial vapour pressures, and the
problem therefore resolves itself into the determina_
tion of the partial vapour pressures of water and
alcohol in the solutions.

The method employed for this purpose was the air_
bubbling method, which has been used extensively by
Perman (Proc. Roy. Soc. 72, 72,(1903); Trans. Far.
Soc. 23, 95, 1927) for the determination of the
vapour pressures of many aqueous solutions, and by
Foote and Scholes (J.A.C.S. 33, 1317,(1911)) and
Dobson (J.C.S. 127 , 2871, (1925)) for the determina_
tion of the partial pressures of water and alcohol
in mixtures of the two. It was thought that this
method would give more accurate relative results
than the distillation method as used by Zawidzki
(Z. fur Ph. Ch. 35, 129,(1900)) in which the sum
of the two partial pressures has to be measured
directly.

The method depends on the fact that when air
is bubbled through a solution, it becomes saturated
with the vapour of each volatile component at its
partial vapour pressure. The weight of each com_
ponent removed therefore, by a known volume of air
can be used to determine these partial vapour pres_
sures.

A/

A volume V of dry air measured at the same temperature $t°C$. as the solution, and at atmospheric pressure, is saturated with the vapours from the solution.

Let w_1 = the weight of water removed as vapour.

w_2 = the weight of alcohol removed as vapour.

P = atmospheric pressure.

t = temperature of the solution

The volume of water vapour, measured under the same conditions as the air, is

$$\frac{w_1}{M_1} \times 22400 \times \frac{(273 + t)}{273} \times \frac{760}{P} \ cc = V_1 \ c.c.,$$

where M_1 is the molecular weight of water.

Similarly the volume of alcohol vapour is

$$\frac{w_2}{M_2} \times 22400 \times \frac{(273 + t)}{273} \times \frac{760}{P} \ c.c. = V_2 \ c.c.,$$

where M_2 is the molecular weight of alcohol.

∴ the total volume of saturated air at temperature $t°C$ and atmospheric pressure P is

$$V + v_1 + v_2$$

where V is the volume of dry air.

Assuming that the ideal gas laws are obeyed, we have as a result of Dalton's law of partial pressures,

$$p_1 = \frac{v_1}{V + v_1 + v_2} \cdot P$$

$$p_2 = \frac{v_2}{V + v_1 + v_2} \cdot P$$

where /

where p_1 is the partial pressure of water in the sol-
ution & p_2 is the partial pressure of alcohol in the
solution.

This calculation is not quite exact, for the
saturated air is not quite at the pressure of the
atmosphere. The difference, however, is very small,
for in the first experiments, a manometer was
attached at the end of the bubbler, just over the
surface of the liquid, and the pressure registered
was only about 1 - 2 m.m. of mercury. The reason
for discarding the manometer, however, was not because
the pressure was small, but because it was difficult
to read, owing to slight oscillations of the mercury.

In this method of determining vapour pressures,
an error may be introduced as a result of solution
of air in the liquids. The solubility of air in
water at 25°C is 16.71 c.c. (at NTP) per litre
(Seidell, "Solubilities of Organic and Inorganic
Substances" 2nd Ed. p.19.), while in absolute
alcohol, air is soluble to the extent of 110 c.c.
(at NTP) per litre ("Dictionary of Solubilities"
Comey 1896, p.2.). In salt solutions these
solubilities are probably lower, for it has been
shown by Geffken (Z. Ph. Ch. 49, 257, 1904) among
others that the solubility of a gas decreases with
increasing salt concentration. These solubilities
are/

are quite considerable, but since the solutions are
made up in presence of air and a preliminary air-
bubbling is always carried out, it is practically
certain that they are saturated with air before the
actual bubbling is commenced.

An error may also arise from the possible
deviation of the vapours from the ideal gas laws.
From a comparison, however, of the vapour pressure
results obtained by this method with those obtained
by the distillation method, as used by Zawidzki
(Z. Phys. Ch. 35, 129, 1900) and others, it appears
that the assumption of conformability to the laws
of perfect gases is quite justified. For example,
Dobson's values for the partial pressures of water
and alcohol in mixtures at 25°C. (J.C.S. 127, 2871,
1925) are in good agreement with those obtained by a
distillation method by Dornte (J. Phys. Chem. 33,
1309, 1929). Perman has also pointed out (Trans.
Far. Soc. 24 330, 1928.) that the vapour pressures
of cane sugar solutions are the same whether deter-
mined by an air-bubbling method or by a static method
in which the vapour over a liquid is examined directly.

In this investigation, moreover, the absolute
values of the partial pressures are not so important
as the relative values, and even if a constant error
were involved in the method, it would have little
effect/

effect on the changes in the partial pressures due to
the addition of an electrolyte.

The concentrations of lithium chloride used were
0.5 m., 1.0 m., and 4.0 m., where m represents
moles per 1000 gms. of solvent.

EXPERIMENTAL.

I. PREPARATION OF MATERIALS.

(a) Alcohol. Commercial Absolute Alcohol was allowed to stand over freshly burned quick_lime for a week in a stoppered flask, the contents being shaken every day. It was then refluxed on a water bath for eight hours, and finally distilled slowly using an eight_bulb fractionating column, and reject_ing the first and last portions (Danner, J.A.C.S., 44, 2832, 1922). All corks used were protected from alcohol vapour by tin foil, and during refluxing and distilling, the alcohol was protected from atmospheric moisture by calcium chloride tubes. The middle portion of the distillate was collected and stored in a brown_coloured Winchester having a tightly fitting glass stopper. The alcohol was further protected from the atmosphere by having a rubber cap tied tightly over the stopper.

The alcohol had a density of D_4^{25} = .78498 and a refractive index of n_D^{20} = 1.36145.

(b) Lithium Chloride. This was prepared from a Kahlbaum preparation which was shown by analysis for chlorine content to correspond fairly accurately to

Li Cl, H_2O. This was dissolved in alcohol and filtered, /

filtered, thus removing most of any other alkali
chlorides which might be present. The greater part
of the alcohol in the solution was then evaporated
off above 50°C. and under reduced pressure. The
anhydrous lithium chloride which separated was quickly
filtered at the pump and transferred to a flask.
It was then dried in the manner described by Pearce
and Hart (J.A.C.S., 44, 2411, 1922) by heating to
170°C. in a stream of pure dry hydrochloric acid gas,
and then heating gently in a stream of pure dry
hydrogen, until the last traces of hydrochloric acid
were removed. The hydrochloric acid gas was generated
from "A.R." sulphuric, and "A.R." hydrochloric, acids,
and was dried by bubbling through concentrated sul-
phuric acid and then passing over phosphorous pent-
oxide contained in a long inclined tube.

The lithium chloride so prepared was kept in
a vacuum dessicator over phosphorous pentoxide. On
analysis for chlorine content it gave a percentage of
chlorine of 83.58. (Theory = 83.61%).

II. APPARATUS.

The apparatus used consists essentially of
three parts having as their functions,
(a) the measurement of the volume of air used,
(b) the complete saturation of the air with the
    vapours of the solution, and

(c)/
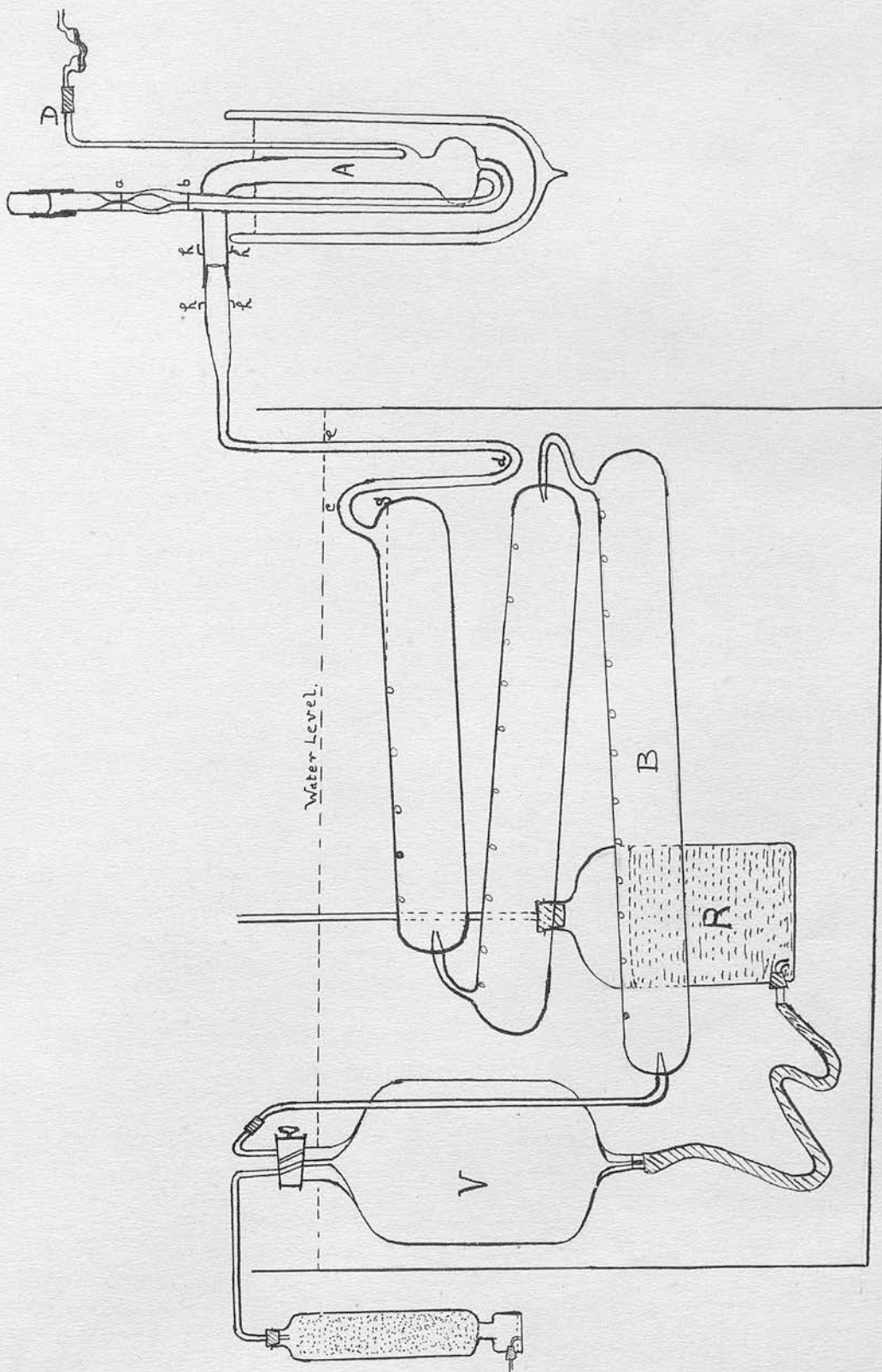
Fig 1.

out. (c.f. Downes and Perman, Trans. Far. Soc. 23, 95, 1927) At the point e the air is saturated with the vapours of the solution at the temperature of the thermostat. Beyond e, the exit tube from the bubbler is kept hot by electrically heated mats to prevent condensation.

The capacity of the bubbler is about 200 c.c. and hence no appreciable change in the composition of the solution is made by the small amount of evaporation produced.

The determination of the weights of water and alcohol in this volume of saturated air presented great difficulty, and several methods were tried before a suitable one was evolved.

In the first method, the air was passed through a combustion tube containing copper oxide, and the products, (carbon dioxide and water), absorbed and weighed in the usual manner. From the weight of carbon dioxide the weight of alcohol was calculated. The weight of water to which this would give rise on combustion was calculated,and the difference between the total weight of water and this weight gave the weight of water carried by the air. From solutions which were highly concentrated in alcohol, the amount of water carried over was too small to be determined accurately by this method and so a physical method was tried.

The /

The air, saturated with water and alcohol, was
passed through a tube surrounded by carbon dioxide
snow to condense out the vapours. The percentage
alcohol in the small quantity of liquid (0.1 - 0.2
gms.) so obtained, was measured by finding its
refractive index with a Zeiss dipping refractometer.
For some unexplained reason, however, consistent
results could not be obtained with this instrument
for mixtures strong in alcohol, while quite reproduc-
ible results were given by mixtures containing under
40% alcohol. For this reason then, as much as pos-
sible of the condensed liquid was run into a weighed
tube and the weight found. A weighed amount of water
was added, and the percentage alcohol determined in
this diluted solution from its refractive index.
From this it was possible to calculate the weights
of water and alcohol respectively in the original
condensed liquid.

This dilution, however, greatly increases the
possible error, and small differences in the relative
amounts of water and alcohol can not be detected by
this method.

The problem of determining the weights of water
and alcohol in the vapour was ultimately solved by a
method depending on the viscosity of water-alcohol
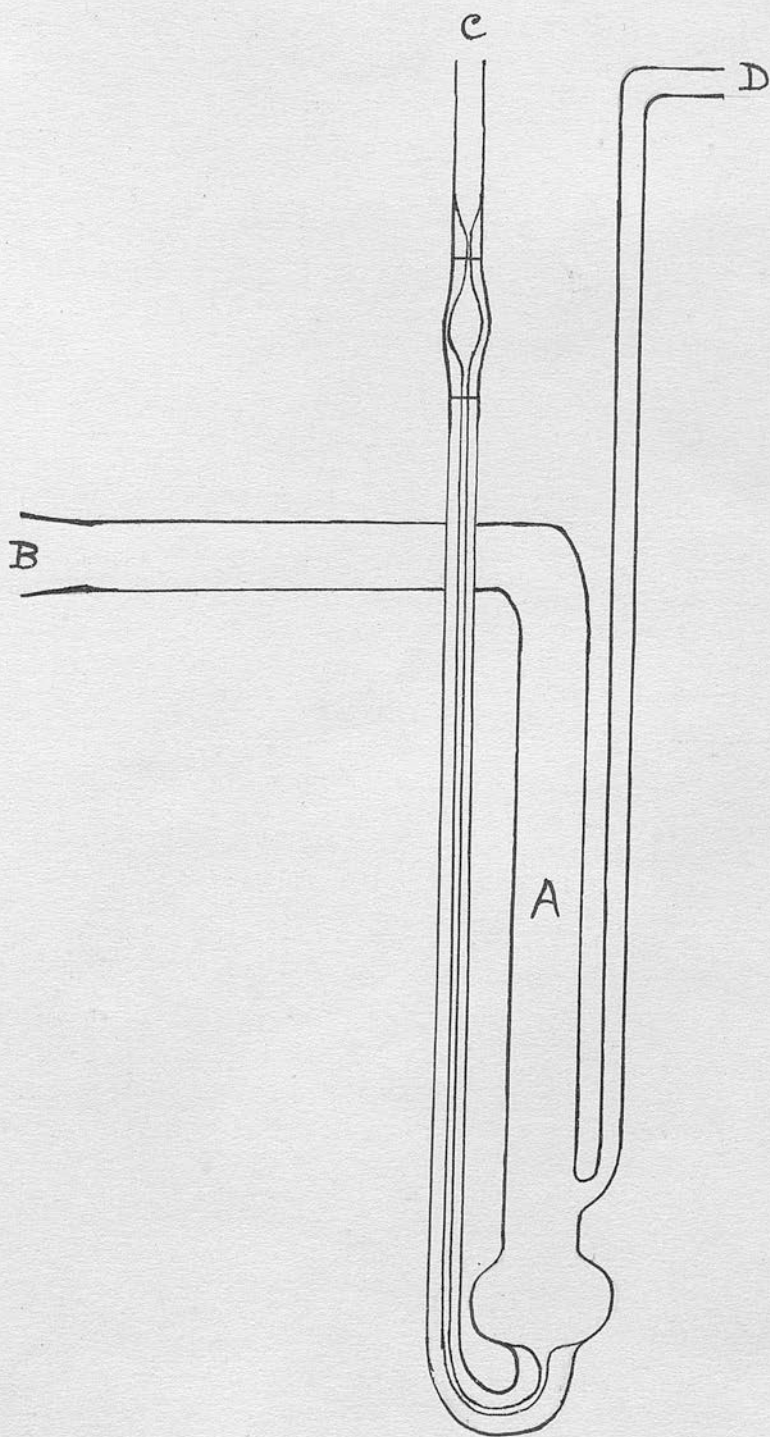mixtures.

The /

Fig 2.

The air was passed through the tube A, shown
in fig (1), which was connected to the heated exit
from the bubbler by a tightly-fitting ground-glass
joint without grease of any kind. The two parts of
the apparatus were held firmly together by wire tied
round the glass hooks h.   The tube A was surrounded
by carbon dioxide snow in a Dewar flask, and the
condensed vapours collected in the bulb at the foot
of A. By weighing the tube before and after an
experiment, the combined weight of water and alcohol
was obtained.

The construction of the tube is shown better in
fig (2).

To determine the percentage of alcohol in the
condensed liquid, the tube was tightly stoppered at
B (fig (2)), and clamped in the thermostat, (which
was constructed of plate glass), in the position
shown. The liquid was sucked up the fine capillary,
till the meniscus was past a , and then allowed to
flow back. The time for the meniscus to go from a
to b was found by a stop-watch, and, since the
capillary had previously been calibrated with known
percentages of alcohol, the percentage alcohol in
the liquid was read directly from a graph.

The capillary ends in a very flat bulb in order
to reduce to a minimum any effect due to small
differences in the volumes of liquid, with consequent
small/

small differences in the effective length of the capillary.

In this method, the liquid is practically un-exposed to the atmosphere, and so there is very little chance of the absorption of moisture. The method of analysis is quick, and it is accurate to at least 0.1%. In the region near pure alcohol it is certainly better than this, probably of the order of 0.05%.

III.   PROCEDURE:-

Each solution was made up by weight from absolute alcohol, distilled water, and lithium chloride. The bubbler was filled with the solution to be exam-ined, as quickly as possible from a tap-funnel, placed in position, and attached to the air vessel which was full of dry air. The heating mats were then attached and the reservoir raised. By cautiously opening the two-way tap in the direction of the bubbler, air was started bubbling through the solution, and this stream of air was continued for about ten minutes to ensure that the apparatus was in the same state at the end as at the beginning of an experiment.

The tube A was weighed after standing in the balance for half an hour after being wiped. It was closed at C (fig (2)) by a piece of glass rod fitting into a piece of rubber tubing, and a small calcium chloride/

chloride tube was attached at D, so that when carbon dioxide snow was placed round the tube, dry air would be sucked in.

The preliminary air-bubbling was stopped, and the tube A attached. The Dewar flask was slipped into position, and filled with carbon dioxide snow. The calcium chloride tube at D was replaced by a small pulsimeter, and the heating mats extended to the bend in the tube A.

By lowering R, and opening the tap slightly towards the drying towers, the vessel V was again filled completely with dry air. When the tap was fully open, the level of the mercury in R was adjusted to be in line with an etch-mark on the capillary at the bottom of V.   The atmospheric pressure was read from the laboratory barometer.

The tap was closed and R raised. When the air pressure in V had become steady, the tap was opened cautiously and the actual air-bubbling com- menced. The rate of bubbling was adjusted by the tap until one bubble passed through the pulsimeter every two seconds. The reason for this slow rate was not so much to secure complete saturation of the air, for as shown by Perman (Proc. Roy. Soc. 72, 72, 1903) this is attained much more quickly, but to give the vapours ample time to condense in A.
At completion of the bubbling, the mercury just reached/

reached under the tap with the latter fully open.

The tube A was disconnected, removed from the Dewar flask, and, after being stoppered at B , allowed to stand for about five minutes. It was then closed at all points, and carefully wiped. After standing in the balance for half an hour, the stoppers were removed with as little handling as possible, and the tube weighed.

It was then stoppered tightly at B and placed in the thermostat as in fig. (2). At c was attached a rubber tube, with a calcium chloride tube at the end. Through this the liquid was sucked up the capillary and the time of flow found, the mean of ten results being taken. By reference to the curve for the calibration of the viscosimeter the percentage alcohol in the liquid was found.

At least two experiments were carried out for each solution.

For the 98 and the 95 mole % alcohol series, a different method was used, in order to obtain greater accuracy in the analysis of the condensed vapours. The total weight of liquid carried over by the volume V was found as before. To find the percentage alcohol, another experiment was carried out, in which from nine to ten litres of air were bubbled through the solution and from one to two gms. of liquid obtained. In this method the air was sucked through the /

the solution by means of an aspirator attached through
a calcium chloride tube to the collecting tube.
(c.f. Perman, Proc. Roy. Soc. 72, 72, 1903).

An interferometer was used to determine the per_
centage alcohol in the liquid so obtained. The
instrument had previously been calibrated by placing
water_alcohol mixtures of known composition in one
cell, and absolute alcohol in the other, and finding
the readings at which the two spectra coincided.
From these results a calibration curve was drawn,
which, over the region required (98% _ 100% by weight
of alcohol), was a straight line. The liquid, ob_
tained in an experiment, was compared with absolute
alcohol in the same way, and from the observed reading,
the percentage alcohol was read from the graph, with
an accuracy of about 0.01%.

The thermostat was electrically heated and con_
trolled, the temperature remaining constant to
$\pm 0.01^{\circ}C$.

R E S U L T S.

CALIBRATION OF APPARATUS :-

(1) Volume of V.

Weight of mercury contained by vessel at $12^{\circ}C$ = 10,496.6 gm.

Density of mercury at $12^{\circ}C$. = 13.5658 gms/c.c. (Landolt_Börnstein Tabellen, 5th Ed. p.77)

$\therefore$ Volume of vessel = 773.7 c.c.

(2) Calibration of Viscosimeter.

For the purpose of calibration, about .15 c.c. of alcohol_water mixtures of known percentage alcohol were placed in the tube, and the time of flow found by means of a stop_watch, the mean of 10 successive readings being taken. Two samples of each mixture were examined in this way. The mean times of flow for the two samples rarely differed by more than $\frac{1}{5}$ ".
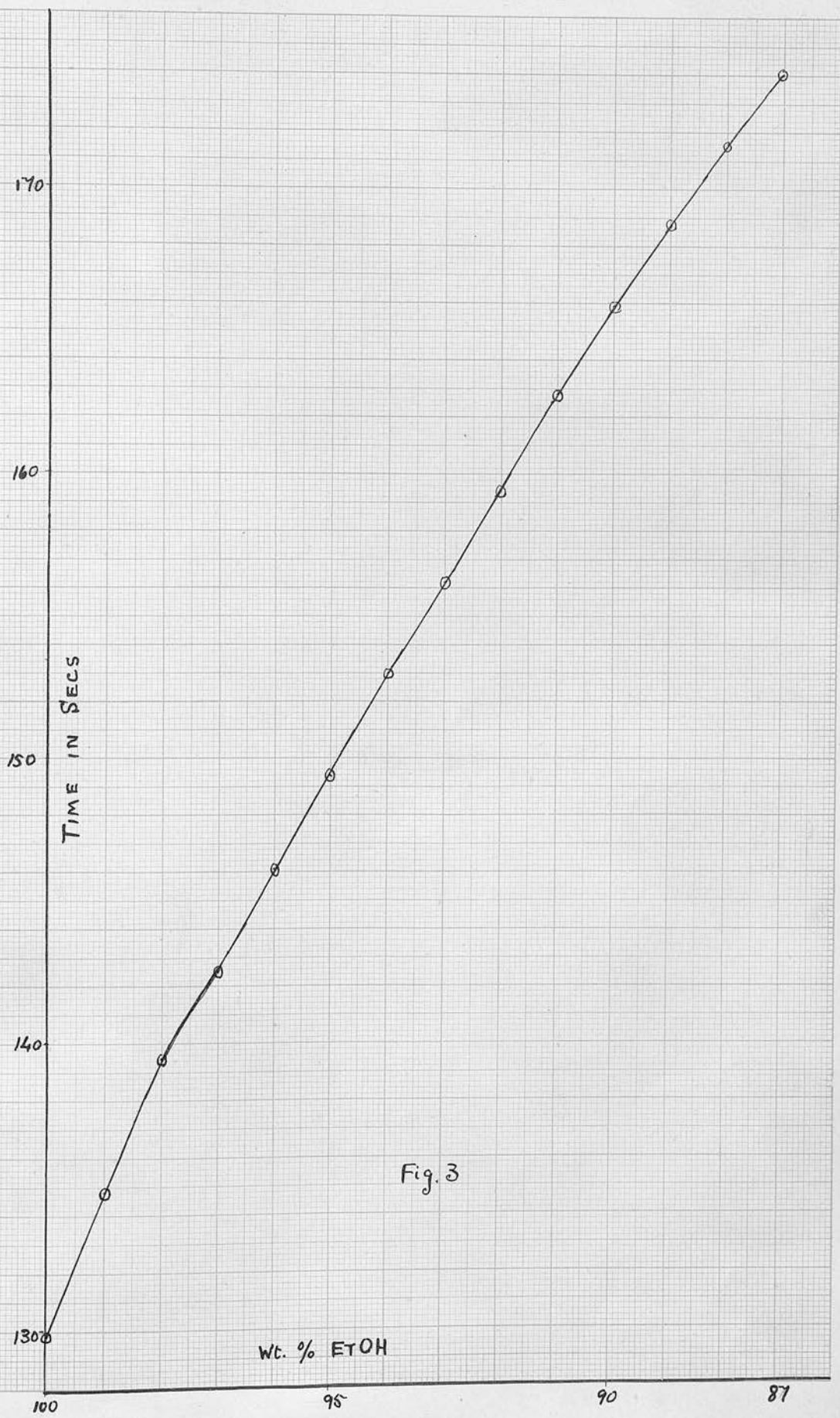
Table I gives the results of this calibration at $25^{\circ}C$.
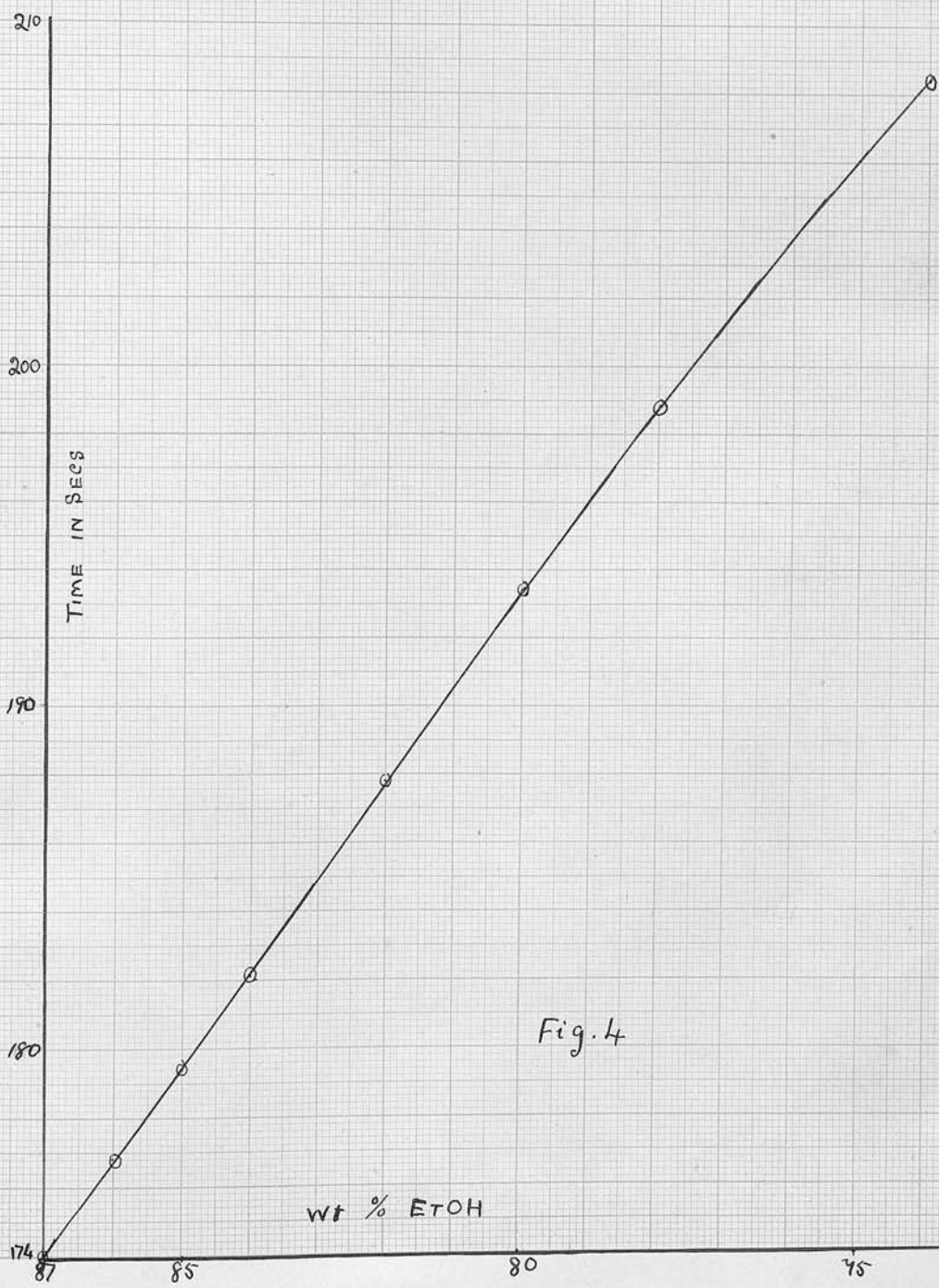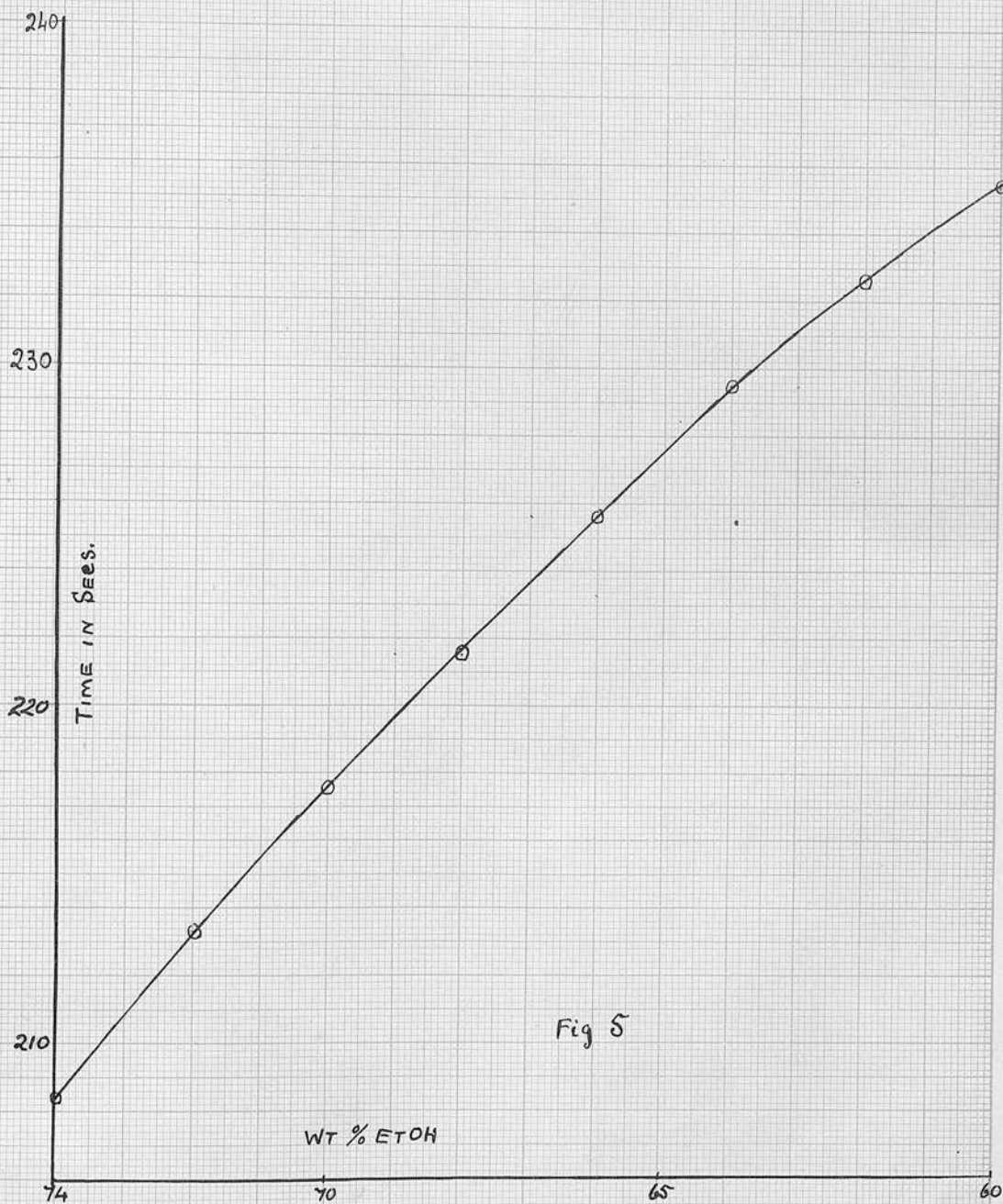
TABLE I./

Fig. 3

Wt. % ETOH

220

Fig. 4

Y-axis: Time in Secs (210, 200, 190, 180, 174)
X-axis: Wt % EtOH (87, 85, 80, 75)

Fig 5

TABLE I.

Wt.% Et.OH	Time of Flow	Wt.% Et.OH	Time of Flow.
100	$2'\ 9\frac{4}{5}''$	86	$2'\ 56\frac{4}{5}''$
99	$2'\ 14\frac{4}{5}''$	85	$2'\ 59\frac{2}{5}''$
98	$2'\ 19\frac{1}{2}''$	84	$3'\ 2\frac{1}{10}''$
97	$2'\ 22\frac{1}{2}''$	82	$3'\ 7\frac{4}{5}''$
96	$2'\ 26\frac{1}{10}''$	80	$3'\ 13\frac{2}{5}''$
95	$2'\ 29\frac{2}{5}''$	78	$3'\ 18\frac{4}{5}''$
94	$2'\ 33''$	74	$3'\ 28\frac{2}{5}''$
93	$2'\ 36\frac{1}{5}''$	72	$3'\ 33\frac{3}{10}''$
92	$2'\ 39\frac{2}{5}''$	70	$3'\ 37\frac{3}{5}''$
91	$2'\ 42\frac{4}{5}''$	68	$3'\ 41\frac{1}{2}''$
90	$2'\ 45\frac{9}{10}''$	66	$3'\ 45\frac{3}{5}''$
89	$2'\ 48\frac{7}{10}''$	64	$3'\ 49\frac{1}{2}''$
88	$2'\ 51\frac{2}{5}''$	62	$3'\ 52\frac{3}{5}''$
87	$2'\ 54''$	60	$3'\ 55\frac{2}{5}''$

By plotting 'wt.% alcohol' against 'time of flow', the calibration curves (Figs.(3) - (5)) were obtained.

(3) Calibration of Interferometer.

The cell of this instrument consists of two compartments A and B. In B we have absolute alcohol and in A, water alcohol mixtures of known composition. With different mixtures in A, different readings are given on the interferometer scale. The /

Fig. 6
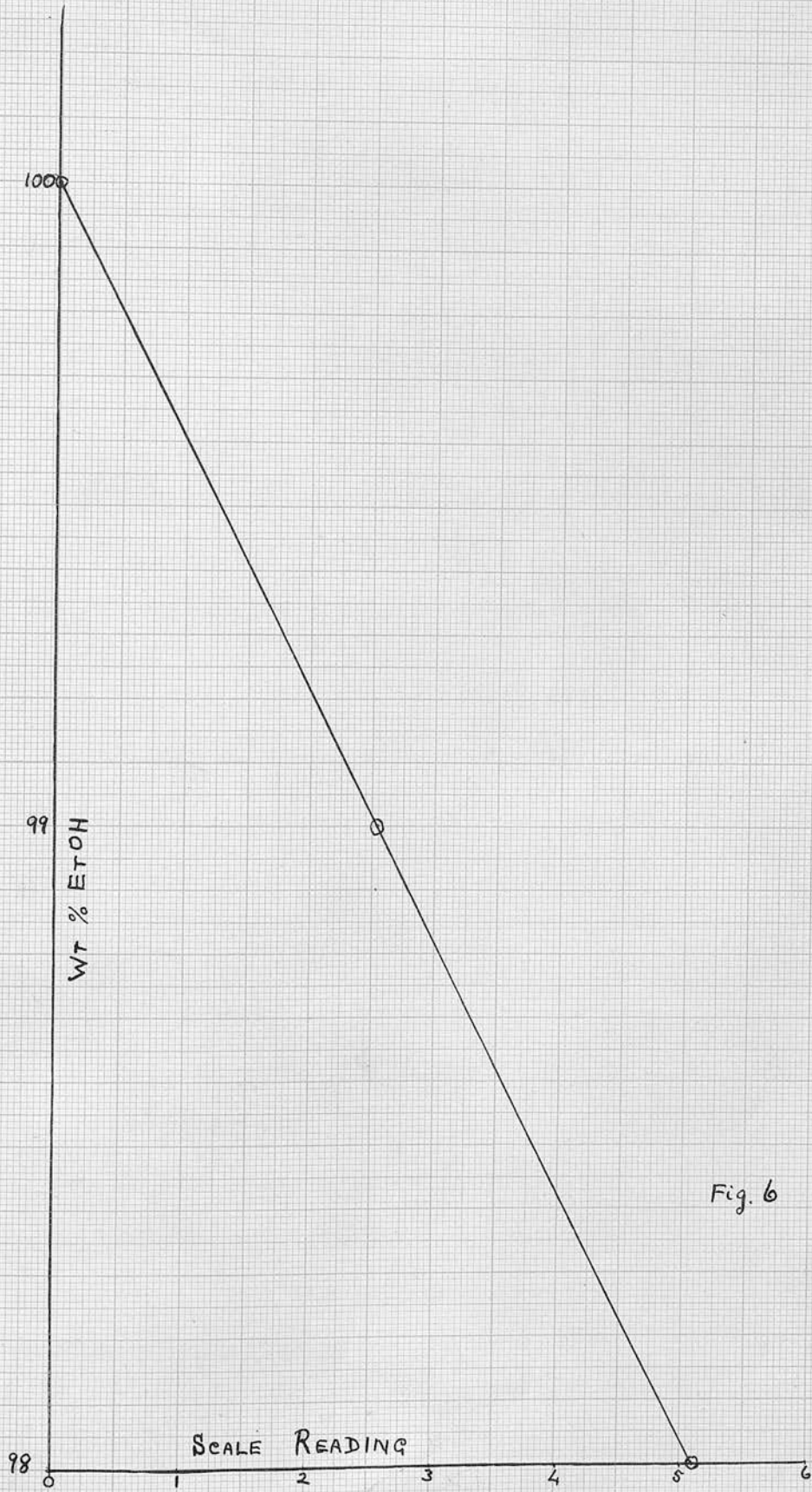
Wt % EtOH

Scale Reading

The following readings were obtained.

100% alcohol in B in each case.

TABLE II.

Wt.% Et.OH in A.	Reading (1)	(2)	Mean.
100	−0.04	+0.05	0.00
99	+2.53	+2.545	+2.54
98	+5.10	+5.12	+5.11

The scale is graduated to .01 of a division.

By plotting "wt.% Et.OH" against "scale reading"
the straight line (fig.6) was obtained.

PARTIAL PRESSURES OF WATER AND ALCOHOL IN SOLUTIONS.

The experimental results are given in table III.

TABLE III.

$$t = 25^{\circ}C.$$

A = Mole % Et.OH in solvent.

m = Conc. of LiCl (moles per 1000 gms. solvent.)

w = Wt. of water + alcohol collected.

P = Atmospheric pressure.

p_w and $p_{alc.}$ are the partial pressures of water and
alcohol respectively.

A	m.	w(gm)	% Et.OH	P m.m.	p_W m.m.	p_{alc} m.m.	Mean p_W	Values. p_{alc}
	0	.1224	100	745	0	58.98	0	58.98
	0	.1224	100	745	0	58.98		
100	0.5	.1190	100	737	0	57.22	0	57.21
	0.5	.1188	100	740	0	57.20		
	1.0	.1123	100	740	0	54.24	0	54.27
	1.0	.1124	100	740	0	54.29		
	4.0	.1066[*]	100	775	0	26.83	0	26.72
	4.0	.1059[*]	100	772	0	26.65		
	4.0	.1060[*]	100	770	0	26.68		
	0	.1205	99.23[1]	752	1.140	57.49	1.141	57.54
	0	.1207		753	1.142	57.58		
98	0.5	.1168	99.37[1]	763	0.908	56.01	0.908	55.98
	0.5	.1167		758	0.907	55.94		
	1.0	.1118	99.43[1]	747	0.787	53.74	0.788	53.78
	1.0	.1120		750	0.789	53.82		
	4.0	.1078[*]	99.60[1]	746	0.277	26.98	0.277	26.96
	4.0	.1076[*]		758	0.276	26.94		
	0	.1183	98.43[1]	756	2.285	56.01	2.286	56.03
	0	.1184		752	2.287	56.04		
	0.5	.1149	98.72[1]	750	1.813	54.66	1.816	54.73
	0.5	.1152		750	1.818	54.79		
95	1.0	.1102	98.80[1]	759	1.637	52.72	1.636	52.69
	1.0	.1105		757	1.641	52.84		
	1.0	.1098		752	1.631	52.50		
	4.0	.1102[*]	99.18[1]	733	.579	27.40	0.580	27.44
	4.0	.1105[*]		746	.581	27.48		

A	m.	w(gm)	% Et.OH	P m.m.	Pw m.m.	Palc. m.m.	Mean pw	Values palc.
	0	.1129	96.15	753	5.352	52.29	5.381	52.42
	0	.1136	96.13	755	5.411	52.55		
	0.5	.1122	96.70	760	4.566	52.32	4.547	52.26
	0.5	.1119	96.72	760	4.528	52.20		
90	1.0	.1080	97.10	747	3.868	50.67	3.852	50.72
	1.0	.1081	97.13	750	3.835	50.76		
	4.0	.1141*	98.55	751	1.060	28.16	1.062	28.21
	4.0	.1145*	98.55	748	1.063	28.25		
	0	.1083	92.60	740	9.858	48.18	9.815	48.04
	0	.1078	92.63	750	9.790	48.02		
	0	.1077	92.60	740	9.797	47.92		
	0.5	.1061	93.52	765	8.491	47.91	8.491	47.91
	0.5	.1061	93.52	767	8.491	47.91		
80	1.0	.1028	94.25	764	7.323	46.93	7.333	47.00
	1.0	.1032	94.23	756	7.343	47.08		
	4.0	.1223*	96.80	747	2.498	29.55	2.534	29.65
	4.0	.1235*	96.75	727	2.557	29.77		
	4.0	.1229*	96.75	735	2.534	29.64		
	0	.1009	89.60	754	12.94	43.60	12.95	43.62
	0	.1010	89.60	754	12.96	43.63		
	0.5	.1006	90.73	742	11.50	44.04	11.47	44.06
70	0.5	.1007	90.80	744	11.43	44.08		
	1.0	.0991	91.65	748	10.24	43.90	10.19	43.92
	1.0	.0991	91.73	742	10.14	43.93		
	4.0	.1317*	95.00	727	4.18	31.03	4.19	31.13
	4.0	.1324*	95.00	741	4.20	31.23		

A	m	w(gm)	% Et.OH	P m.m.	pw m.m.	Palc. m.m.	Mean Pw	Values. Palc.
	0	.0899	84.47	741	17.26	36.68	17.24	36.65
	0	.0897	84.47	731	17.21	36.61		
	0.5	.0907	86.00	741	15.71	37.74	15.78	37.77
50	0.5	.0910	85.90	733	15.85	37.79		
	1.0	.0905	87.00	745	14.58	38.14	14.53	38.13
	1.0	.0903	87.08	750	14.47	38.11		
	4.0	.1465 *	91.77	769	7.61	33.18	7.65	33.17
	4.0	.1465 *	91.70	770	7.68	33.16		
	0	.1507	79.33	764	19.44	29.16	19.48	29.08
	0	.1505	79.17	735	19.52	29.00		
	0.5	.1545	80.37	739	18.87	30.21	18.84	30.19
25*	0.5	.1541	80.60	740	18.80	30.16		
	1.0	.1562	81.35	741	18.20	30.92	18.18	30.90
	1.0	.1559	81.30	741	18.15	30.86		
	4.0	.1511	86.63	745	12.66	32.08	12.70	32.08
	4.0	.1511	86.55	745	12.73	32.07		
	0	.0839	59.40	740	21.67	12.40	21.62	12.42
	0	.0839	59.60	741	21.57	12.44		
	0.5	.0866	61.40	749	21.27	13.22	21.20	13.24
5*	0.5	.0867	61.70	750	21.12	13.26		
	1.0	.0889	63.85	755	20.44	14.12	20.48	14.13
	1.0	.0891	63.77	750	20.52	14.13		
	4.0	.0986	73.40	751	16.68	18.00	16.66	18.01
	4.0	.0985	73.50	748	16.64	18.01		
	0	.0368 *	0	760	23.77	-	23.77	-
	0.5a				23.45	-	23.45	-
0	1.0a				23.05	-	23.05	-
	4.0a				19.21	-	19.21	-

(*) Volume of air used = 2 V in experiments marked thus.

(1) % alcohol found by means of interferometer.

(a) Values for these solutions deduced from values given in
     Landolt-Bornstein Tabellen, 5th Ed. p.1385).

Fig. 7

m.m. Hg

Mole % Et.OH

Et.OH

H₂O
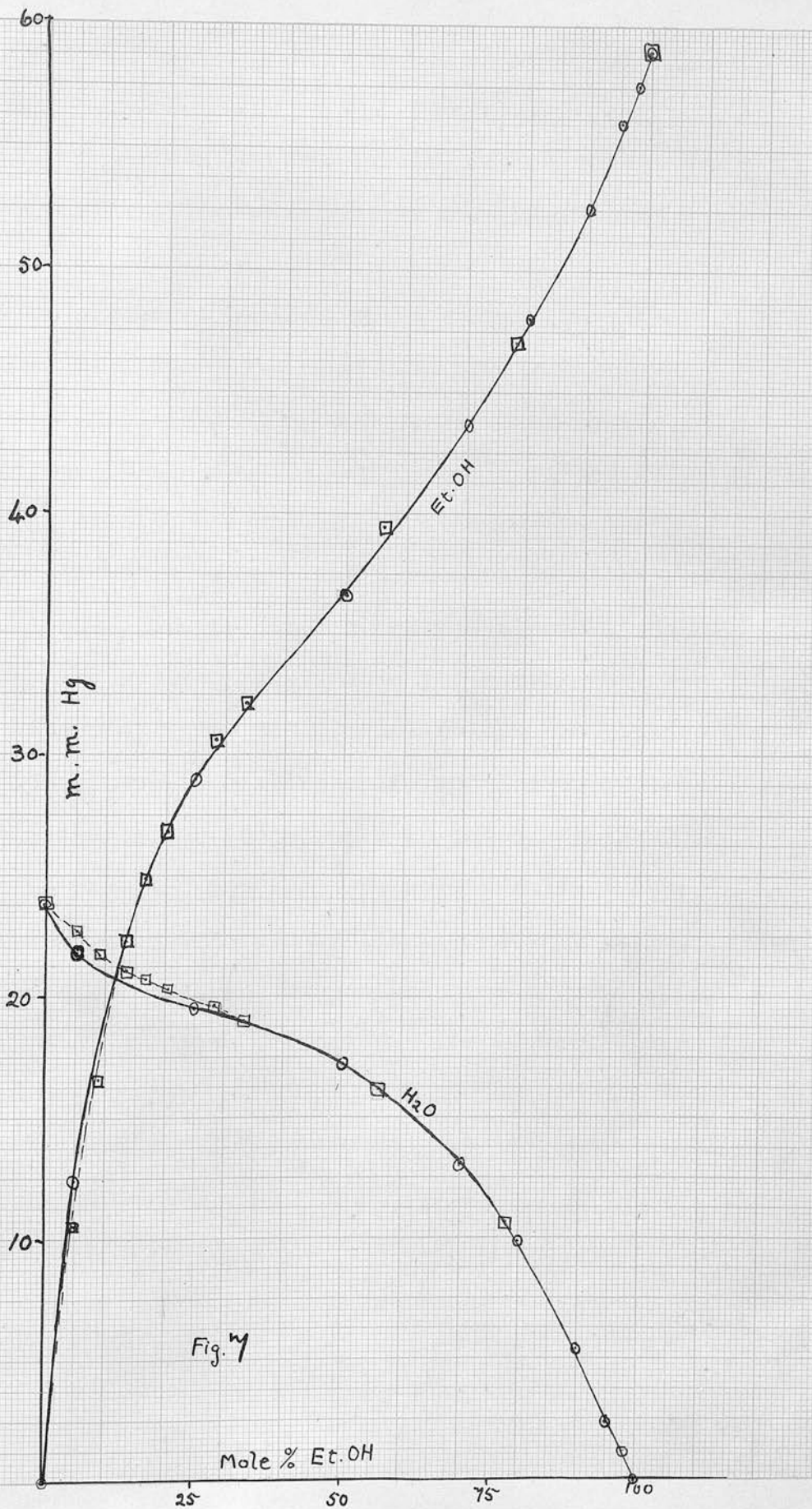
The individual values for the vapour pressures rarely differ from each other by more than about 5 in 1000.

The agreement between these values and those obtained by Dobson, who also used an air-bubbling method (J.C.S. _127_, 2871, 1925), is shown by Fig.(7). The points in the squares are Dobson's values while those in circles are the values obtained in the present investigation. The agreement is good from pure alcohol down to about 30 mole % alcohol. Below this point, however, the values for water are lower than Dobson's, while the alcohol values are higher.

The effect of lithium chloride on the partial pressures of water and alcohol in these solutions is shown in Figs.(8) and (9). To obtain these curves, we have plotted for each series (100 mole % Et.OH, 98 Mole % EtOH, etc.) the partial pressures of water and alcohol respectively against the concentration of lithium chloride.

From the partial pressures of water and alcohol, given in table III, the activities of the two com-ponents are found from the relation

$$\alpha = \frac{p_1}{p_{10}} \, ,$$

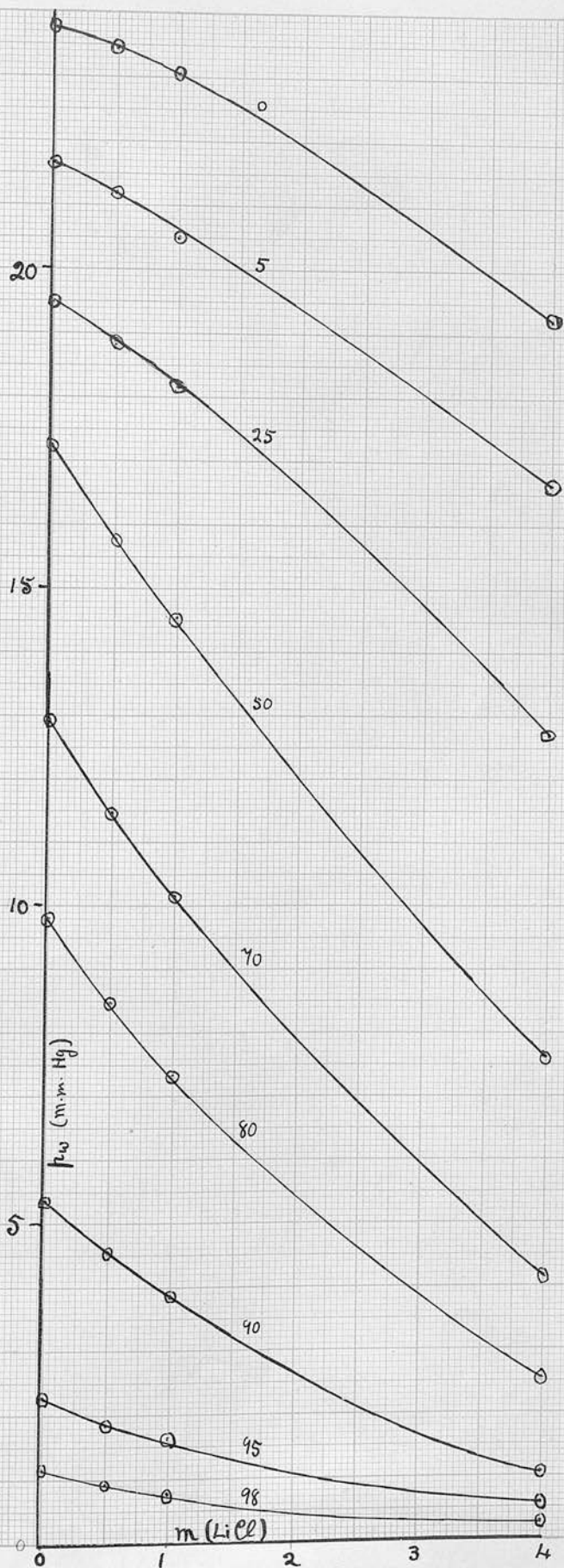where p_1 is the partial pressure of the component in the solution,
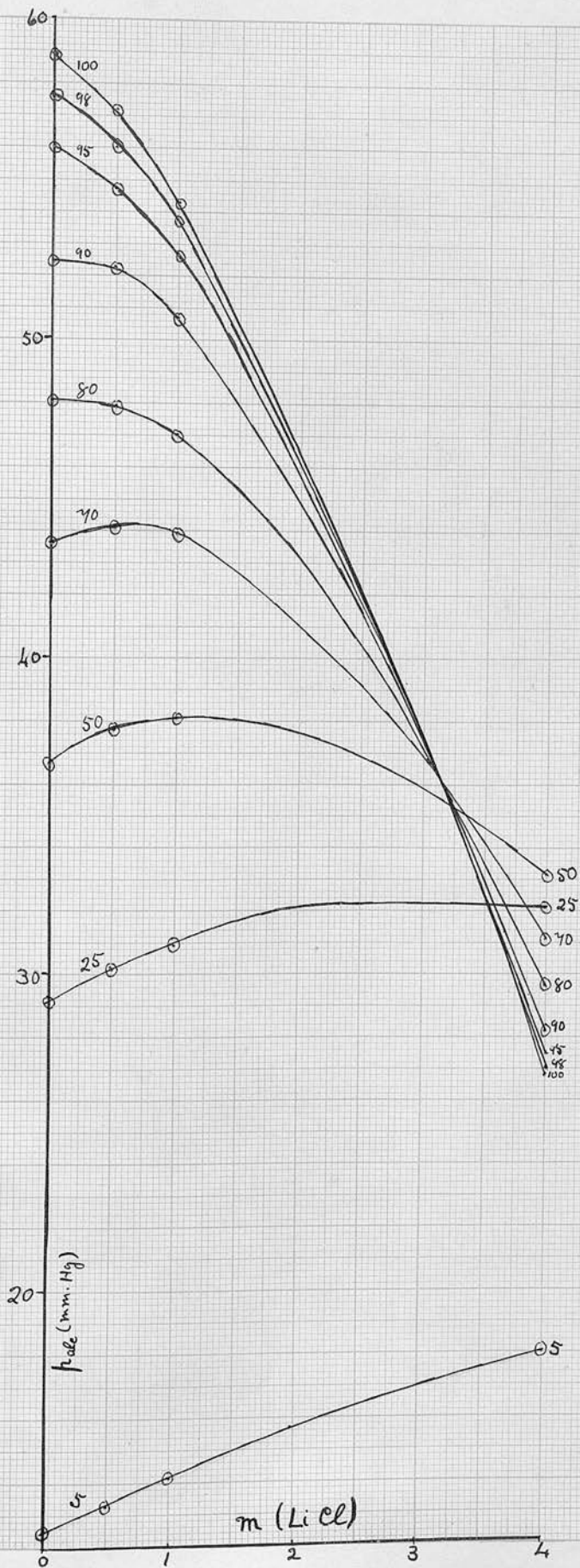
p_{10} /

Fig. 8

Fig. 9

p_{10} is the vapour pressure of the component in the pure state at the same temperature, and α is the activity of the component.

Moreover, if we let α_0 be the activity of a component when no salt is present, then $\left(\dfrac{\alpha}{\alpha_0}\right)$ is the relative activity of the component, referred to the activity of the component in the pure solvent as unity.

Table IV gives the activities and relative activities of water and alcohol in the solutions.

α_w = the activity of water.

$\alpha_{alc.}$ = the activity of alcohol.

TABLE IV.

A.	m.	$\alpha_{alc.}$	$\alpha_w.$	$\left(\dfrac{\alpha}{\alpha_0}\right)_{w.}$	$\left(\dfrac{\alpha}{\alpha_0}\right)_{alc.}$
100	0	1.000	–	1.000	–
	0.5	.9699	–	.9699	–
	1.0	.9202	–	.9202	–
	4.0	.453	–	.453	–
98	0	.9764	.04806	1.000	1.000
	0.5	.9497	.0383	.9727	.795
	1.0	.9118	.03315	.9340	.690
	4.0	.4573	.01165	.4684	.2425
95	0	.9504	.09622	1.000	1.000
	0.5	.9286	.0764	.9770	.794
	1.0	.8940	.06884	.9406	.7155
	4.0	.4654	.02441	.4898	.2537

TABLE IV (continued)

A	m.	α_{alc}	α_w	$\left(\dfrac{\alpha}{\alpha_o}\right)_{alc}$	$\left(\dfrac{\alpha}{\alpha_o}\right)_w$
	0	.8900	.2264	1.000	1.000
90	0.5	.8874	.1914	.998	.845
	1.0	.8611	.1621	.9685	.716
	4.0	.4786	.0446	.538	.197
	0	.8155	.4130	1.000	1.000
80	0.5	.8133	.3573	.998	.8651
	1.0	.7980	.3085	.979	.7470
	4.0	.5033	.1066	.6175	.2581
	0	.7404	.5575	1.000	1.000
70	0.5	.7481	.4829	1.011	.8660
	1.0	.7457	.4282	1.008	.7680
	4.0	.5286	.1763	.7140	.3152
	0	.6223	.7253	1.000	1.000
50	0.5	.6410	.6639	1.030	.9154
	1.0	.6473	.6114	1.040	.8430
	4.0	.5631	.3219	.902	.4438
	0	.4938	.8195	1.000	1.000
25	0.5	.5126	.7928	1.038	.9672
	1.0	.5247	.7649	1.063	.9332
	4.0	.5446	.5344	1.132	.6520
	0	.2106	.9096	1.000	1.000
5	0.5	.2249	.8919	1.068	.9804
	1.0	.2396	.8616	1.138	.9472
	4.0	.3054	.6916	1.481	.7603
	0	-	1.000	-	1.000
0	0.5	-	.9865	-	.9865
	1.0	-	.9696	-	.9696
	4.0	-	.8081	-	.8081

Fig. 10

The curve labels read, from top to bottom on the right side: 0, 5, 25, 50, 70, 80, 95, 98, 90.

The y-axis is labeled $\left(\dfrac{\alpha}{\alpha_0}\right)_w$ with gridmarks at 0, 0.5 and 1.0.

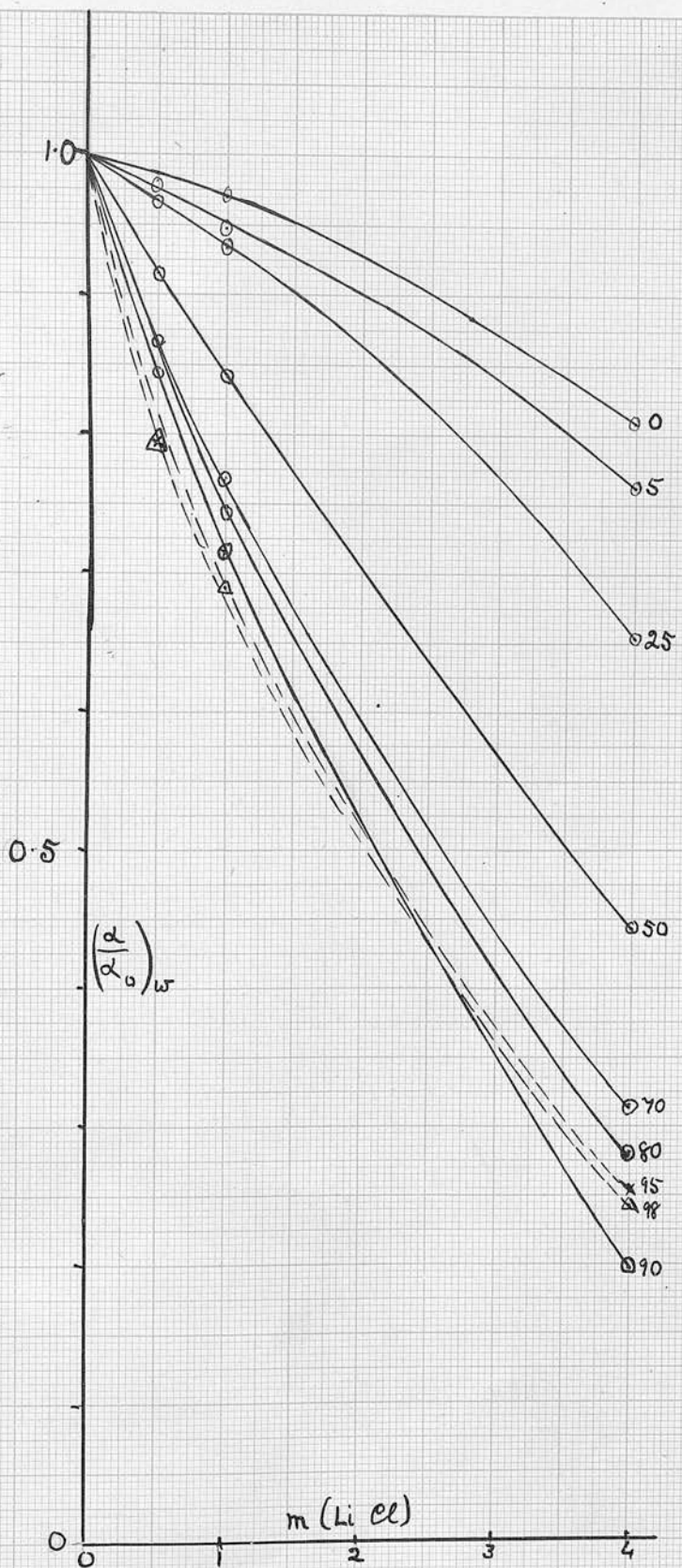The x-axis is labeled $m\,(Li\,Cl)$ with marks at 0, 1, 2, 3, 4.
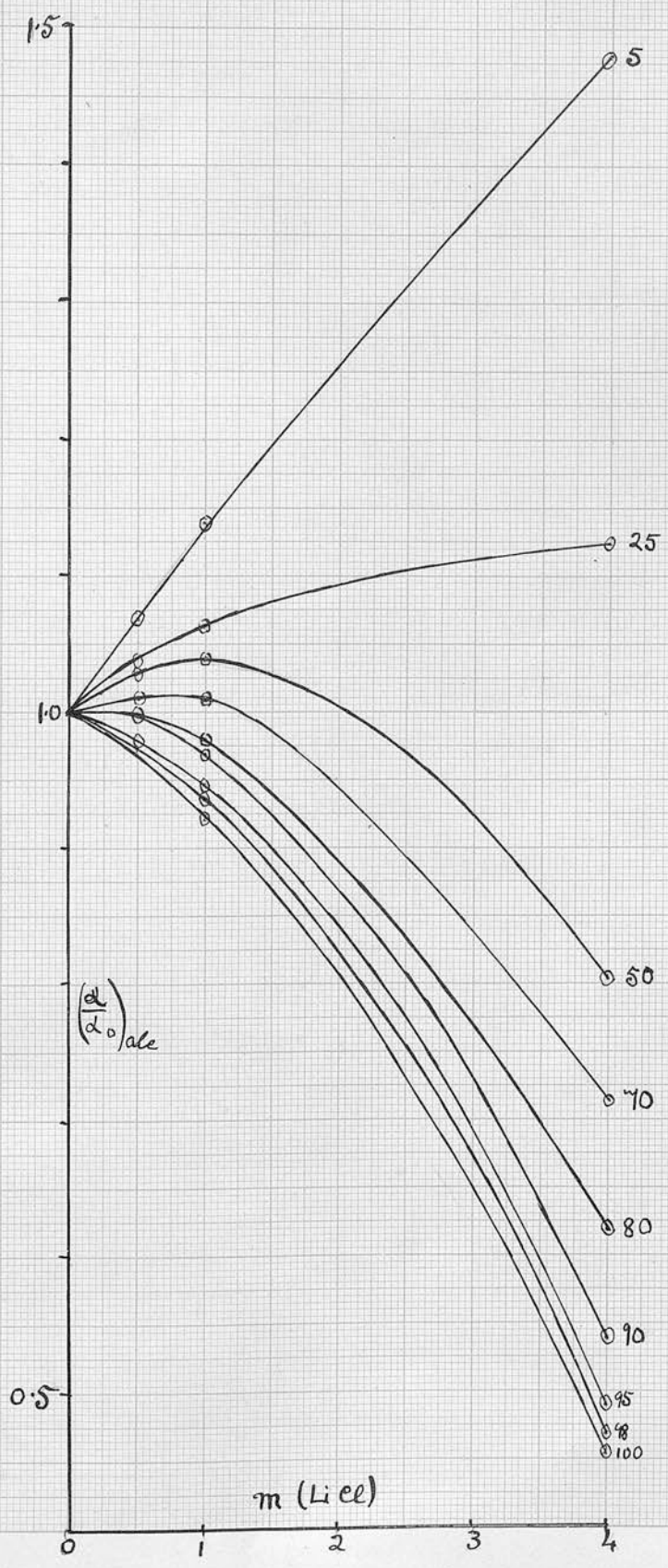
Fig. 11

By plotting $\left(\dfrac{\alpha}{\alpha_o}\right)$ for water and alcohol respect-
ively against the concentration of lithium chloride
in each series (100, 98, etc.) the curves shown in
figs.(10) and (11) were obtained.

The partial vapour pressures of water and
alcohol in certain of the solutions examined at $25^{\circ}C$.
were determined at $35^{\circ}C$. and the results obtained are
tabulated in table V.

TABLE V.

A	m.	$35^{\circ}C.$ P_w	$35^{\circ}C.$ P_{alc}	$(\Delta H)_w$	$(\Delta H)_{alc}$
	0	42.18	–	10,480 cals.	–
0	1.0	40.78	–	10,430	–
	0	35.53	50.51	10,970	10,090 cals.
25	1.0	32.72	54.42	10,730	10,340
	0	31,00	63,90	10,720	10,150
50	1.0	26,64	67,14	11,080	10,340
	0	24,29	76,87	11,490	10,350
70	1.0	18.51	76.90	10,910	10,230
	0	10.20	92.33	11,680	10,340
90	1.0	6.84	89.50	10.490	10,370
	0	–	101.7	–	9,950
100	1.0	–	95.4	–	10,300

The values of ΔH shown in the above table were
obtained from the well known equation connecting
vapour pressure with temperature,
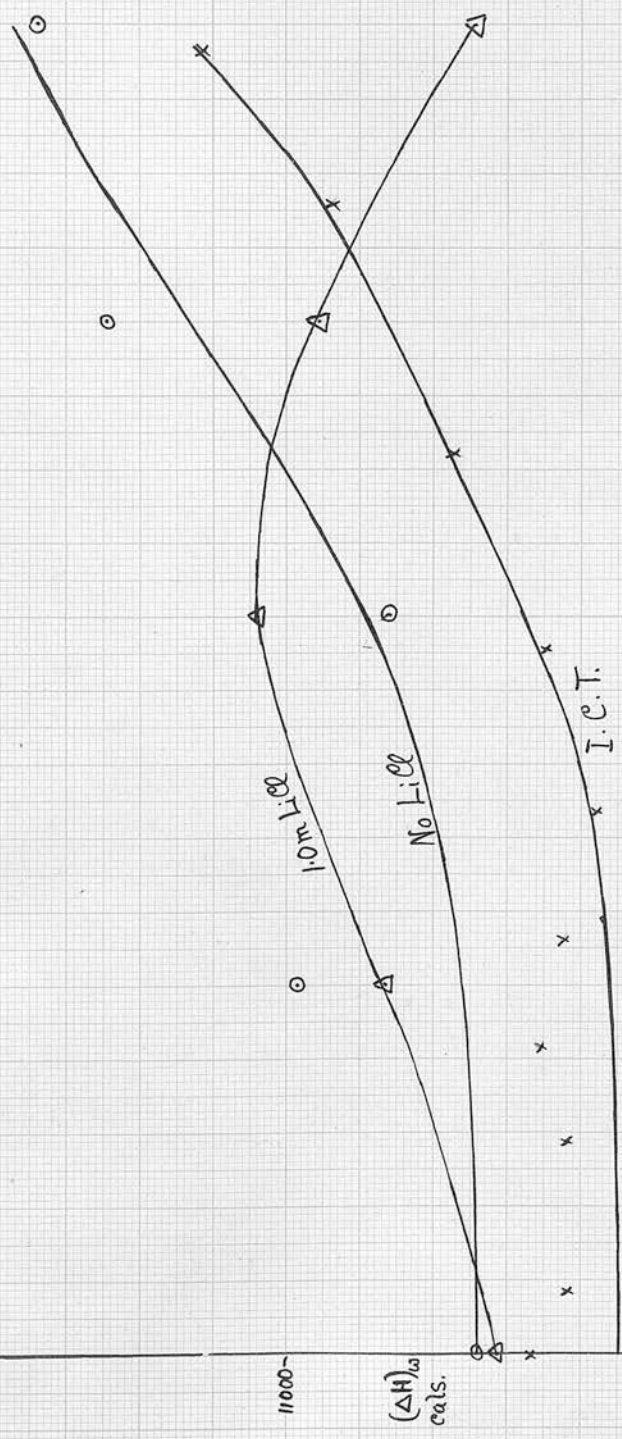
$$\frac{d \log p}{d T} = \frac{\Delta H}{R T^2}$$
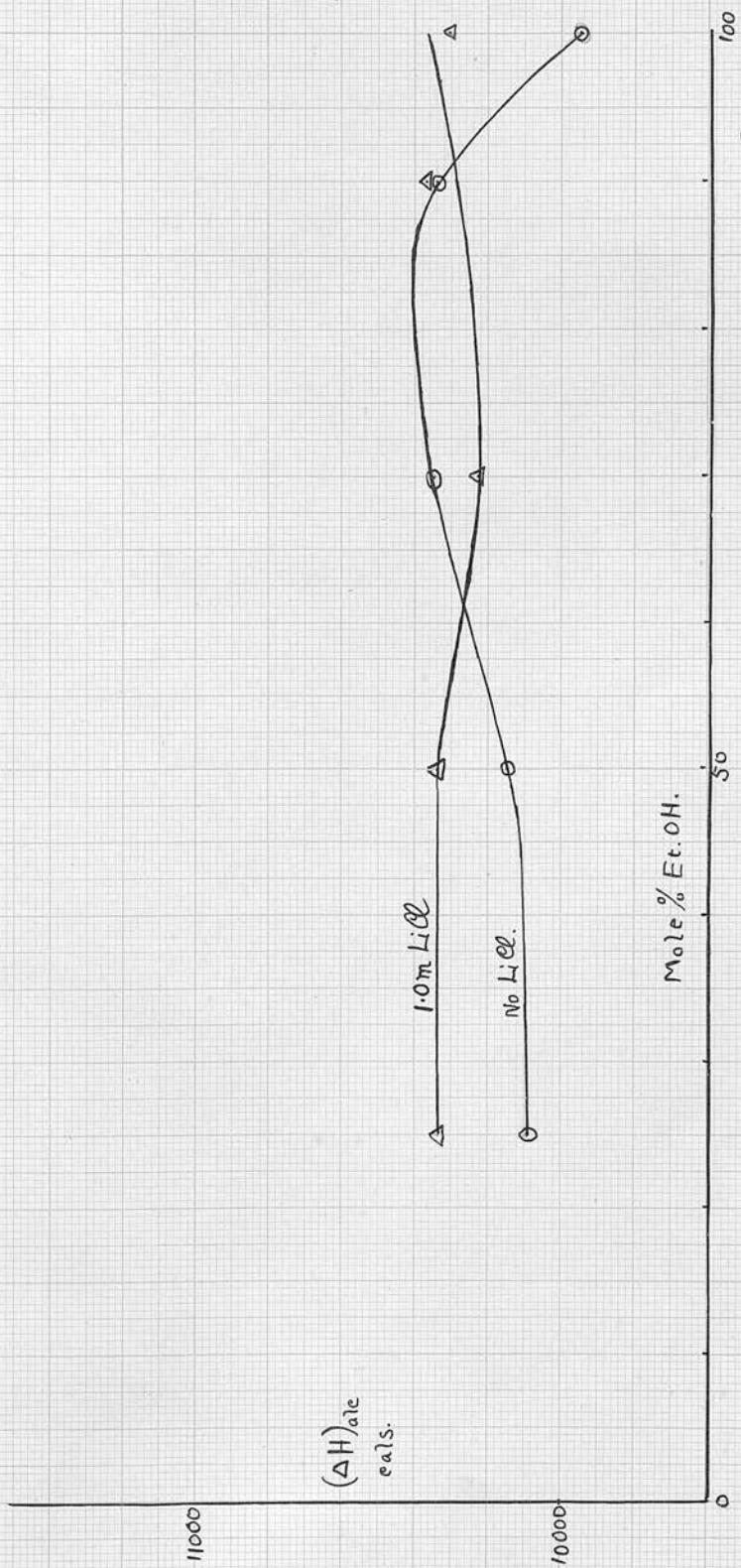
Fig. 12

Mole % Et.OH

$(\Delta H)_{\omega}$ cals.

1.0 m LiCl

No LiCl

I.C.T.

Fig 13

Where p is the vapour pressure of the substance,
T is the absolute temperature, and ΔH is the
latent heat of evaporation per mole of the substance.

On integration, this equation becomes

$$\log p_1 - \log p_2 = - \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right).$$

Substituting in this equation the partial
vapour pressures of water at the two temperatures,
25°C. and 35°C, the latent heats of evaporation of
1 mole of water $\left(\Delta H \right)_w$ in the various solutions
were evaluated. In a similar manner the corresponding
quantities $\left(\Delta H \right)_{alc.}$ for alcohol were obtained.
The curves, shown in figs.(12) and (13), were
obtained by plotting $\left(\Delta H \right)_w$ and $\left(\Delta H \right)_{alc.}$ respect-
ively against the composition of the solvent.

D I S C U S S I O N.

The effect of certain non-electrolytes on the partial vapour pressures of water and alcohol in mixtures has been investigated by Wright, (J.C.S. 121, 2251, 1922), (ibid. 123, 2493, 1923), who correlates the results obtained with the solubility of the non-electrolyte in the individual components. He finds that where the added substance is soluble in water but not in alcohol, or where it is soluble in both components, it raises the vapour pressure of alcohol, and lowers that of water in a mixture; where it is soluble in alcohol only, it generally lowers the vapour pressure of alcohol, and raises that of water to a slight extent. In these experiments, the solvent was of fixed composition, viz. 38% (by weight) of alcohol.

In a later paper (J.C.S. 125, 2068, 1924) Wright studied the effect of various salts, in concentrations of 0.5 m., on the vapour pressures of water - alcohol mixtures, and found, in agreement with his previous work, that the vapour pressure of alcohol was always raised while that of water was always lowered. Here again, the solvent was of fixed composition, viz. 10 mole % alcohol.

The present investigation, however, shows that the effects produced by adding an electrolyte to a mixed solvent vary according to the composition of the /

the latter. Fig.(9) shows that from a composition
of 100 mole % alcohol down to 80 mole % alcohol, the
addition of lithium chloride depresses the vapour
pressure of alcohol. In the 70 mole %, and 50 mole
% series, concentrations of 0.5 m. and 1.0 m lithium
chloride produce a rise in the vapour pressures of
alcohol, while a concentration of 4 m lithium chloride
causes a lowering. Where the solvents are 25 mole %
alcohol and 5 mole % alcohol, a rise in the vapour
pressure is produced by all concentrations of lithium
chloride up to 4 m.

The corresponding curves for water given in
fig.(8), show that the vapour pressure of water is
lowered by the addition of lithium chloride in all
solvents, from 100 mole % water down to 2 mole %
water.

In terms of activities this amounts to the fact,
that the activity of water is lowered in all water-
alcohol mixtures by the addition of lithium chloride,
the lowering increasing with increasing concentration
of electrolyte. In strong alcohol mixtures, the
activity of alcohol is affected in a similar manner.
In weaker alcohol mixtures there is at first a rise
in the activity of alcohol, followed by a lowering at
greater concentrations of lithium chloride, and in
still weaker mixtures, a rise in the activity of
alcohol is produced even by very high concentrations
of electrolyte.

These/

These effects are readily accounted for in a qualitative manner in terms of the relative attrac_ tions of the ions for the two types of solvent mole_ cules. Since water is a more highly polar substance than alcohol, we may assume that the tendency of the ions to hold water molecules is greater than their tendency to hold alcohol molecules. The activity of water will accordingly be lowered in all solvents, and we should expect the lowering to be greater, the smaller the proportion of water, since a greater part of the water available will be attached to the ions. Reasoning on these lines, it was anticipated, indeed, that in solutions which contained 2 moles % of water, its activity would be reduced practically to zero, especially with the higher concentrations of lithium chloride. This, however, was not found to be the case. In these solutions, the activity of alcohol is considerably lowered by lithium chloride, the ions being probably largely solvated by alcohol. It appears that in these solutions, the water molecules are pre_ vented from being taken up completely by the ions by the very large excess of alcohol molecules, this large excess partially compensating the superior attraction of the ions on the water molecules.

It is noteworthy that in all solutions, the electrolyte has a greater relative effect on the water than on the alcohol. This is shown by table VI which gives the fractional lowerings of the vapour pressures of water and alcohol respectively.

In/

In this table Δ is the vapour pressure lowering of a component; p_w and p_{alc} are the vapour pressures of water and alcohol in the pure solvent. $\frac{\Delta}{p}$ is the fractional lowering.

TABLE VI.

A	m	$\frac{\Delta}{p_w}$	$\frac{\Delta}{p_{alc}}$	A	m	$\frac{\Delta}{p_w}$	$\frac{\Delta}{p_{alc}}$
	0.5	.205	.027		0.5	.0821	-.0297
98	1.0	.310	.066	50	1.0	.157	-.0404
	4.0	.757	.532		4.0	.556	.095
	0.5	.206	.023		0.5	.0329	-.0382
95	1.0	.285	.059	25	1.0	.0667	-.0626
	4.0	.746	.512		4.0	.348	-.1034
	0.5	.155	.0031		0.5	.0194	-.0676
90	1.0	.284	.0324	5	1.0	.0527	-.138
	4.0	.803	.462		4.0	.230	-.450
	0.5	.135	.0027		0.5	.0135	-
80	1.0	.253	.0217	0	1.0	.0303	-
	4.0	.742	.383		4.0	.192	-
	0.5	.114	-.0101				
70	1.0	.213	-.0069				
	4.0	.676	.286				

That the effect of lithium chloride on the activity of water does become more pronounced as the proportion of water decreases is shown by fig. (10). The only discrepancies are found at a concen-tration/

concentration of 4 m in the series 95 and 98 moles %
alcohol, both of these points lying above the cor_
responding point for 90 mole % alcohol. From a con_
sideration of fig.(14), however, it appears that
these may not be real divergencies, for there is an
approximate linear relationship between $\left(\frac{\alpha}{\alpha_0}\right)_w$ and
the composition of the solvent for the 0.5 m and
1.0 m series while for the 4 m series the relation_
ship is also approximately linear from 0 up to
90 mole % alcohol, beyond which this sudden deviation
appears. These abnormal values may therefore be due
to experimental error in the determination of the
very small vapour pressures of water in these solu_
tions.

As the solvent becomes richer in water, the water
has a better chance of entering the ionic electric
fields, and its greater polarizability as compared
with alcohol soon makes itself felt by excluding
alcohol molecules to an ever increasing extent from
this region. The lowering of the activity of alcohol
therefore becomes smaller and smaller as the alcohol
content of the solvent diminishes, as is shown by
fig.(11), until a point is reached at which the
addition of lithium chloride produces a rise in the
activity of alcohol.

The quantitative working out of these conceptions
gives rise to great mathematical difficulties, and a
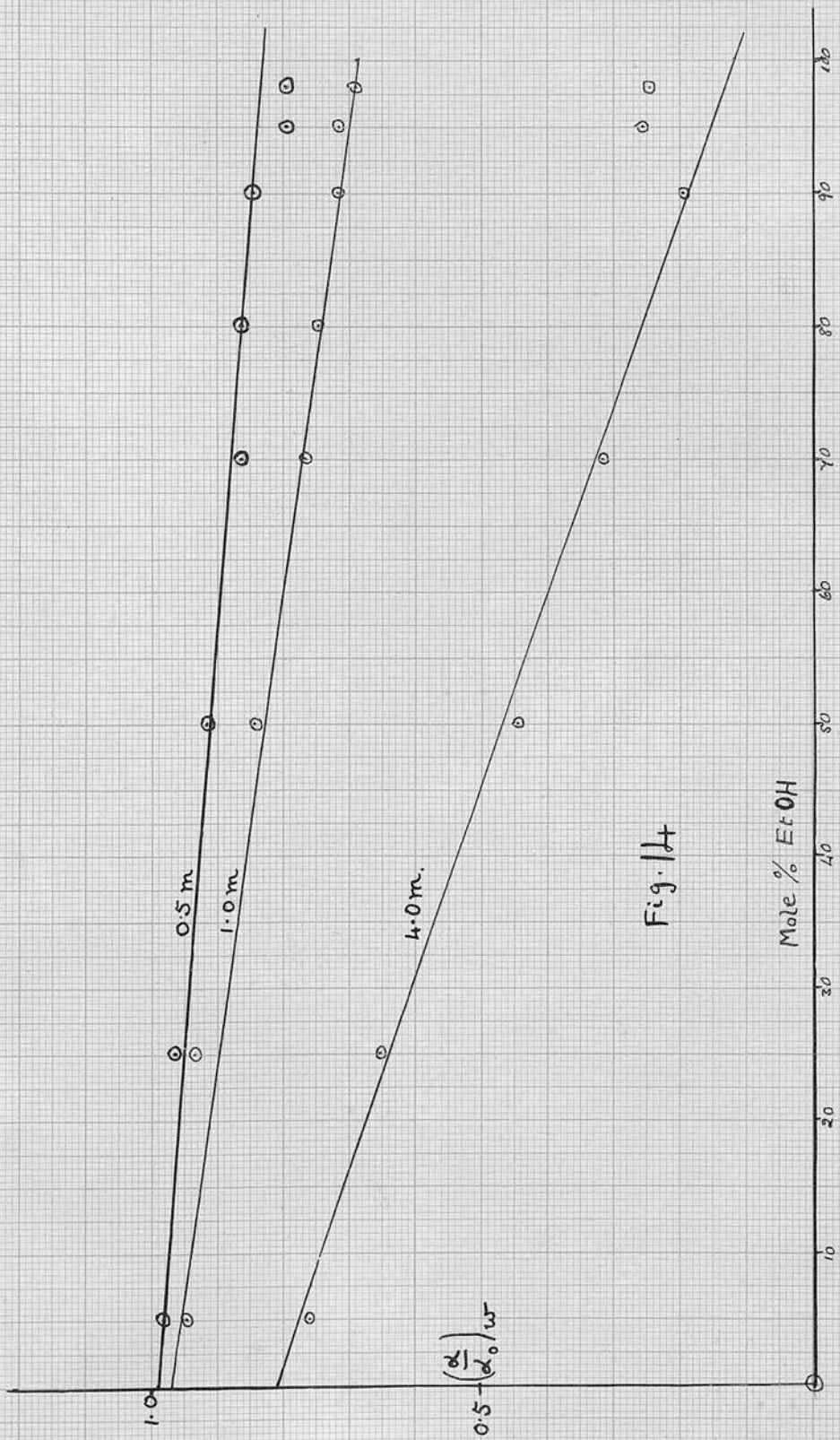complete theoretical treatment of the subject has
not/

Fig. 14

0.5 m

1.0 m

4.0 m.

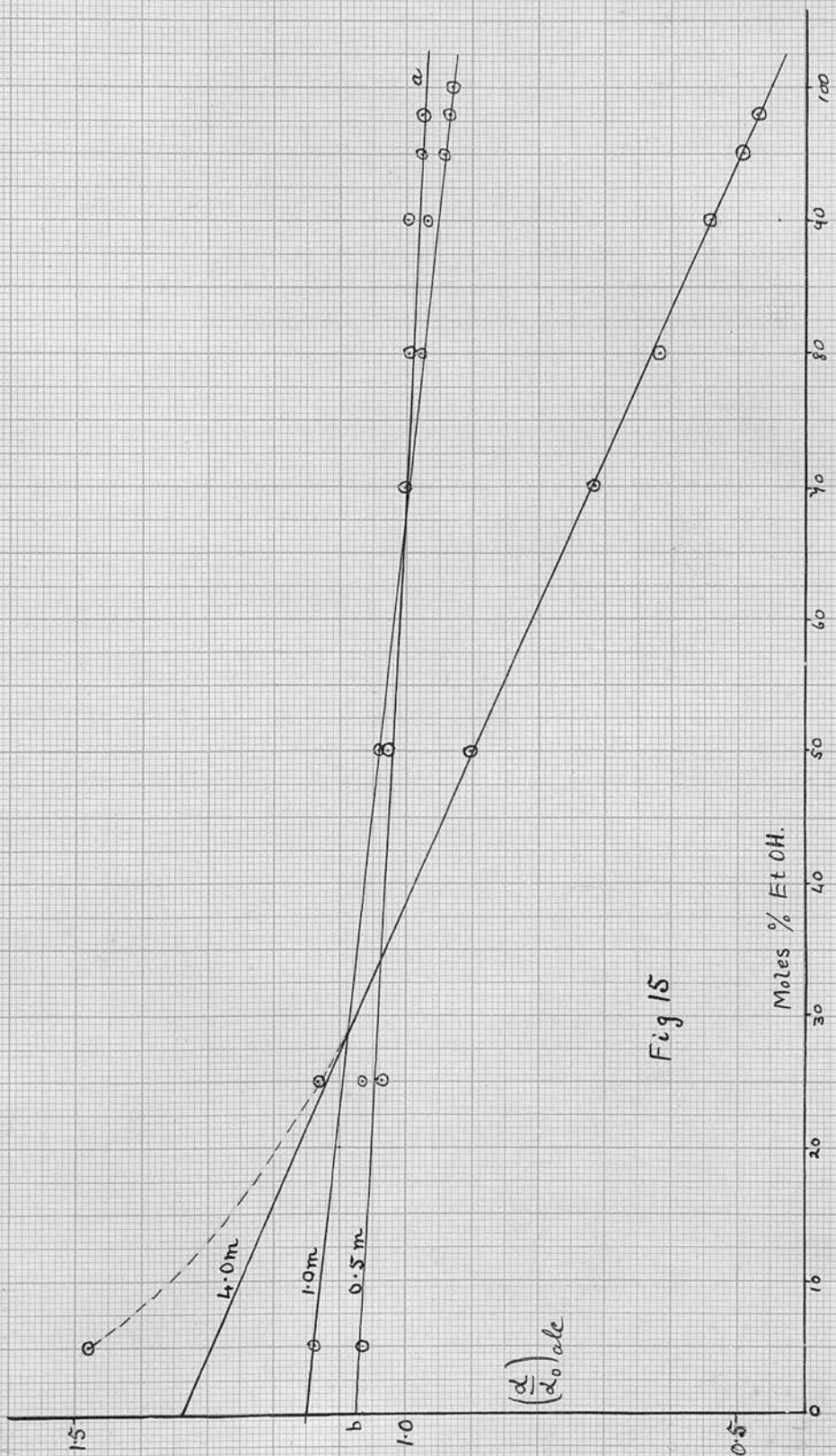$\frac{m}{\left(\frac{\gamma}{\gamma_0}\right)}$

1.0

0.5

Mole % EtOH

Fig 15

not been attained. It may be noted that the theory, as developed by Debye and Hückel, of the activities of strong electrolytes in a single solvent, from which the activities of the latter can easily be obtained, is only formally successful. The precise nature of the terms expressing the interaction be- tween ions and molecules is still uncertain, and the extension to mixed solvents involves quantities which are still unknown.

The results given above, exhibit the important relationship, that the relative activities of both water and alcohol, at constant concentrations of lithium chloride, are nearly linear functions of the molar fraction of alcohol in the solvent. This is illustrated in figs. (14) and (15) in which $\left(\frac{\alpha}{\alpha_o}\right)_w$ and $\left(\frac{\alpha}{\alpha_o}\right)_{alc}$ are plotted against M_{alc} for each concentration of lithium chloride.

It follows that the results can be expressed by equations of the types,

$$\left(\frac{\alpha}{\alpha_o}\right)_{alc} = M_{alc}\, f_a\,(m) \;+\; M_w\, f_a^{\,1}\,(m)$$

and $\left(\frac{\alpha}{\alpha_o}\right)_w = M_w\, f_w\,(m) \;+\; M_{alc}\, f_w^{\,1}\,(m)$

$f_a(m)$ and $f_w(m)$ are functions of the salt concentration, representing the effects of salt on pure alcohol and pure water respectively.

$f_a^{\,1}(m)$ and $f_w^{\,1}(m)$ represent the changes in the relative activities produced by the addition of

alcohol/

alcohol, and of water, molecules.

For each concentration of lithium chloride, the best straight lines were drawn in figs.(14) and (15), and produced to cut the ordinates denoting zero alcohol and zero water.

Considering the 0.5 m concentration in fig.(15) it is seen that the term $M_{alc} f_a$ (m) is represented by the point a which is 0.97. Since M_{alc} is 100, then f_a (m) is .0097. The term $M_W f_a^1$ (m) is represented by b which is 1.075, and hence f_a^1 (m) is .01075.

In a similar way, the values of these functions are found for the 1.0 m and 4.0 m concentrations.

By carrying out the same processes for the water curves, the functions f_w (m) and f_w^1 (m) are found for the three concentrations.

These functions are shown in table VII.

TABLE VII.

	0.5 m	1.0 m	4.0 m
f_a (m)	.0097	.0093	.0045
f_a^1 (m)	.01075	.0115	.0134
f_w (m)	.0099	.0097	.0081
f_w^1 (m)	.0083	.0069	.0012

The equations given above, therefore, become for the 0.5 m concentration

$$\left(\frac{\alpha}{\alpha_o}\right)_{alc} = .0097\ M_{alc} + .01075\ M_W$$

$$\left(\frac{\alpha}{\alpha_o}\right)_w = .0099\ M_W + .0083\ M_{alc}.$$

The equations for the 1.0 m and 4.0 m concentra-
tions are obtained by using the corresponding constants.

From these equations the relative activities of
water and alcohol in the various solutions were
calculated, and the correspondance between these
calculated values and the observed values is shown
in tables VIII and IX.

Calculated and observed values of $\left(\dfrac{\alpha}{\alpha_0}\right)_{alc.}$

TABLE VIII.

Mole % $E_T OH$	0.5 m calc.	obs.	1.0 m calc.	obs.	4.0 m calc.	obs.
5	1.070	1.068	1.140	1.138	(1.296)	1.481
25	1.050	1.038	1.097	1.063	1.117	1.132
50	1.023	1.030	1.040	1.040	0.895	0.902
70	1.003	1.011	0.996	1.008	0.718	0.714
80	0.992	0.998	0.974	0.979	0.628	0.618
90	0.981	0.998	0.952	0.968	0.539	0.538
95	0.975	0.977	0.941	0.941	0.495	0.490
100	0.970	0.970	0.930	0.920	0.450	0.453

TABLE IX. /

Calculated and observed values of $\left(\dfrac{\alpha}{\alpha_o}\right)_w$.

TABLE IX.

Mole % EtOH.	0.5 m calc.	obs.	1.0 m calc.	obs.	4.0 m calc.	obs.
0	0.990	0.987	0.970	0.970	0.810	0.808
5	0.983	0.980	0.9565	0.947	0.776	0.760
25	0.951	0.967	0.9005	0.933	0.638	0.652
50	0.910	0.915	0.830	0.843	0.465	0.444
70	0.878	0.866	0.774	0.768	0.327	0.315
80	0.862	0.865	0.747	0.747	0.258	0.258
90	0.846	0.845	0.719	0.716	0.189	0.197
95	0.838	0.794	0.705	0.715	0.154	(0.254)

From these tables it is seen that there is approximate agreement between the observed and calculated values.

Within the limits of agreement of the data with the above equations, the effects of lithium chloride on water-alcohol mixtures are completely summed up in fig.(16) in which the functions f_a (m), f_w (m), f_a^1 (m) and f_w^1 (m) are plotted against the salt concentration. f_w (m) and f_w^1 (m) refer to the relative activities of water in 100% water and in 100% alcohol, respectively, the activity of water in any mixed solution at a given salt concentration being obtained by applying, according to the mixture rule, the molar fractions of the two components in the solvent to these curves. f_a (m) and f_a^1 (m)
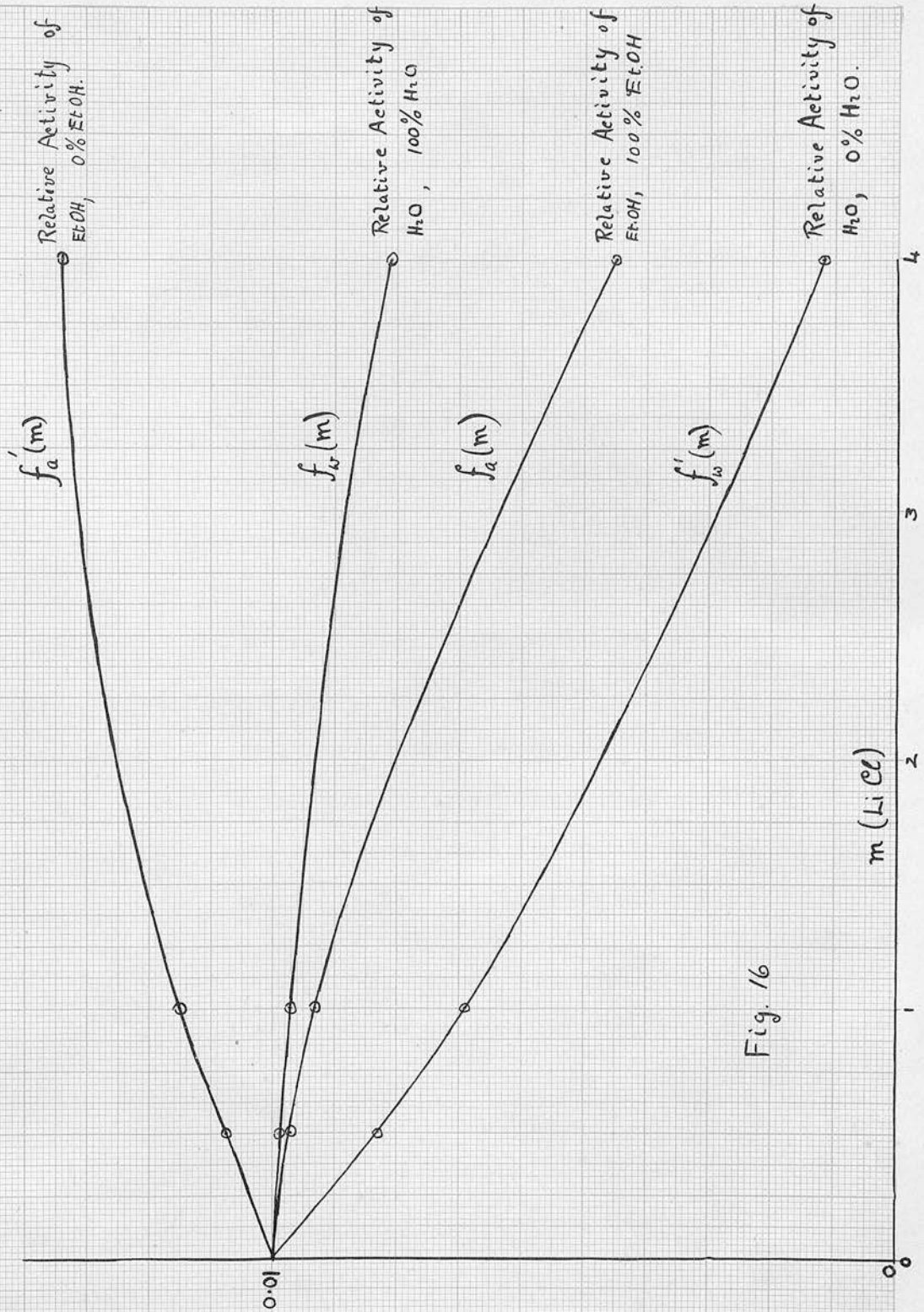
refer/

Fig. 16

refer to alcohol, and the same rule applies.

It can be seen that the effect of the addition of water on the relative activity of alcohol, is represented by $M_w f_a^1 (m)$, which can be regarded as a measure of the salting-out effect. The important conclusion is thus reached, that the salting-out effect is a function, not only of the salt concentration, but also of the molar fraction of water. In studies on salting-out in dilute solutions, where M_w remains nearly 1, this factor has hitherto been overlooked. $f_a^1 (m)$ can be regarded as the reduced salting-out effect, and, at a given salt concentration, has the same value in all mixtures, with the possible exception of the solution containing a large quantity of salt and a small proportion of alcohol, in which the observed value deviated considerably from the linear relation.

LATENT HEATS OF EVAPORATION.

The curves which have been obtained in figs.(12) and (13) for the variation of the latent heats of evaporation of water and alcohol with the composition of the solvent, do not appear to be very conclusive. For comparison, in the case of water, the curve, deduced from similar data at $20^\circ C$. and $40^\circ C$. given in the International Critical Tables Vol.III, p.290, is shown.

No/

No general conclusions can be drawn by comparing the curve obtained with no lithium chloride with the corresponding curve where lithium chloride is present at a concentration of 1 m. It appears strange that, where there is very little water present, it seems to be easier for water to leave the solution of lithium chloride than to leave the pure solvent.

In the case of alcohol, the latent heat of evaporation does not appear to vary to any great extent between the compositions of 25 mole % alcohol and 90 mole % alcohol, but again no general con_clusions can be drawn from these curves.

On account of the difficulty of determining with sufficient accuracy, the temperature coefficients of the vapour pressures of water and alcohol in these solutions, it is exceedingly difficult to obtain accurate values for ΔH , and so no very great reliance can be placed on these curves.

S U M M A R Y.

(1) An air-bubbling method has been devised for
     the determination of the partial pressures of
     water and alcohol in mixtures, in which the
     volume of air required is less than a litre.

(2) The partial vapour pressures of water and
     alcohol have been measured at 25°C, in mixtures
     containing no solute and in mixtures containing
     lithium chloride at concentrations of 0.5 m,
     1.0 m, and 4.0 m. Similar measurements have
     been made at 35°C. with a concentration of
     1.0 m and also with no solute.

(3) It has been shown that, in water-alcohol mixtures,
     lithium chloride lowers the activity of water,
     while it may either lower or raise that of
     alcohol, depending on the composition of the
     solvent and the concentration of lithium chloride.
     The fractional lowering, in the case of water,
     is always greater than that in the case of
     alcohol.

(4) An approximately linear relation has been
     established between the relative activities of
     both water and alcohol, and the molar fraction
     of alcohol in the solvent.

(5)/

(5)   The latent heats of evaporation of water and
      alcohol in mixtures containing no electrolyte,
      and in mixtures with lithium chloride at a
      concentration of 1.0 m as solute, have been
      calculated, but these results do not appear to
      be very significant.

      In conclusion, I wish to express my thanks to
Dr J.A.V. Butler for his deep interest in the work,
and for his many valuable suggestions.