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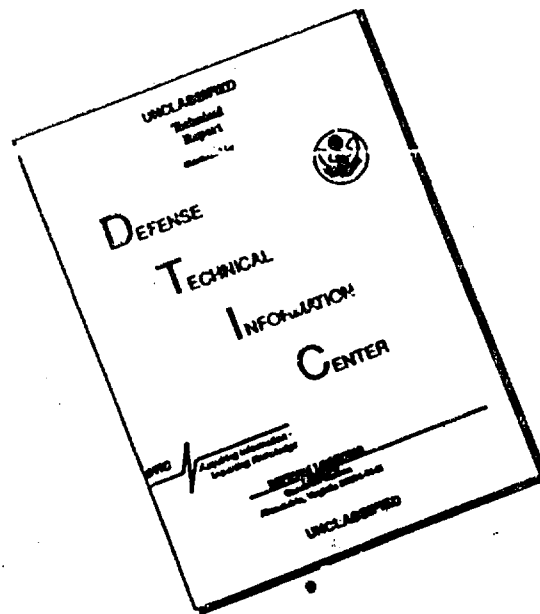
P.T.P. 528

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# THE DETERMINATION OF FREE BASE IN STABILISED GB.

By

E. NEALE

## PORTON TECHNICAL PAPER No. 528

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The Determination of Free Base in

Stabilised GB

by

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## SUMMARY

In view of possible loss of triethylamine from stabilised GB during filtration under reduced pressure the need has arisen for a method of determining the free base in the charging. A simple colorimetric method of estimating triethylamine has been developed and applied to the measurement of partial pressure of the base in low mole fractions over GB. Some information on the equilibria between triethylamine and the various acidic impurities in GB has been obtained by the same technique.

The deviations from ideality shown by the triethylamine/GB system are of practical interest in demonstrating that the volatility of the base will be greater than would be expected from the vapour pressure of the pure material.

The data on acid-base equilibria emphasise the desirability of keeping the acidity of GB low rather than relying too much on its 'neutralisation' by added base.

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## The Determination of Free Base in

## Stabilised GB

by

### E. Neale

## Introduction

Although triethylamine is one of the most effective agents for 'neutralising' the acidic impurities in technical GB, and has for some time been accepted as the stabiliser for GB produced in this Country, there are certain difficulties associated with its use in large scale production;

(a)  Some of the impurities (e.g. hydrochloric acid) form salts with triethylamine which are insoluble in GB, thus necessitating a filtration system in the plant.

(b)  The volatility of triethylamine is such that any free base in the stabilised charging may be partly lost by evaporation when the material is filtered under reduced pressure.  It is of course desirable to maintain a slight excess as further acidity may develop from hydrolysis or other decomposition in storage.

The primary object of the work reported below was to develop a simple method of determining excess triethylamine in GB which could be applied to the stabilised material after filtration.  The investigation was subsequently extended to obtain information on acid-base equilibria in GB.

## Choice of method

Reaction between the weaker acidic impurities and triethylamine is an equilibrium process:

$$Et_3N \ + \ HA \ \rightleftharpoons \ Et_3NH^+ \ + \ A^-$$
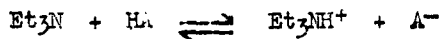
Any direct chemical analysis of the charging is therefore precluded as removal of triethylamine will shift the equilibrium towards the left.  As triethylamine is volatile however, a possible method of approach is to measure its partial pressure in the system since the salts formed may be regarded as involatile.  Ideally the pressure should be measured by a physical method which does not disturb the equilibrium but this is difficult in practice;  a good approximation may be obtained however by removing a vapour sample for analysis provided the amount of triethylamine in the vapour phase is small compared with that in the liquid.

- 1 -

peak is at $5100 \text{A}^{\circ}$. This afforded a simple colorimetric method of estimating microgram quantities. The presence of GB in the chloroform had no effect nor was the presence of small amounts of water sufficiently serious to justify any special measures to dry the chloroform. Details of procedure are given in Appendix 1 with a calibration curve as Fig.2.

## Materials

(a) **Technical GB** (SH.238) prepared at Sutton Oak by the 'di-di' process and stored in varnished steel for some years. Apparent acidity 490 p.p.m. This material was chosen to represent the worst possible acidities which might be encountered in stored commercial GB, though it is, of course, not representative of present production.

(b) **Pure GB.** from the technical grade - twice distilled giving an apparent acidity less than 1 p.p.m.

(c) **Triethylamine.** Hopkins and Williams product dried over barium oxide $N_D^{20} = 1.4001$. Diethylamine content not more than 0.1 per cent.

(d) **Acidic Materials.** Methyl phosphonofluoridic acid was prepared and purified (at the Ministry of Supply Establishment, Nancekuke) shortly before use. Methylphosphonic dichloride and isopropyl methylphosphonochloridate were distilled under reduced pressure as required. Methylphosphonic difluoride was distilled at atmospheric pressure over diethyl aniline. Methylphosphonic acid and its isopropyl half-ester had been prepared and purified some months before but were stored in a desiccator.

In view of the difficulty of adding known amounts of dry HF to GB, equimolar amounts of dry isopropanol and pure methyl phosphonic difluoride were added to GB containing an excess of triethylamine:

$$\text{MePOF}_2 + \text{Pr}^i\text{OH} + x\,\text{Et}_3\text{N} \longrightarrow \text{MePO(F)OPr}^i + \text{HF}. x\text{Et}_3\text{N}.$$

Analysis of a sample by the Peroxide method modified for elimination of $\text{MePOF}_2(5)$ showed that the conversion was quantitative within the limits of the analytical method.

## Results

The partial pressure of triethylamine over pure GB at various low mole fractions is shown graphically in Fig.3. Results obtained by the static and dynamic methods are compared with the theoretical curve for the system obeying Raoults' law. In calculating the latter, the vapour pressure data of Thompson and Linnett (6) are used.

It will be noted that there is a marked positive deviation from Raoults' Law. The fact that results by the dynamic method are somewhat higher than those by the static method needs some comment. A test with triethylamine alone in the dynamic apparatus gave a recovery equivalent to a saturated vapour concentration of 350 mg/l. The value calculated from the published vapour pressure data is 305 mg/l; the discrepancy may be due to adsorption of vapour on the surface of the glass. The static method is not open to this objection; here results are not likely to be high unless the air contains liquid droplets - this is improbable as similar results were obtained after passage through a glass wool filter. Furthermore the curve obtained by the static method may

- 3 -

be expressed well by an equation of the Duhem-Margules type for a binary liquid system:

$$p'_A = p^o_A \ x_A \ E^{\alpha x_B^2}$$

where $x_A$ and $x_B$ are the mole fractions of solute and solvent and $p^o_A$ is the vapour pressure of the pure solute. In the present case the constant $\alpha$ has a value of 1.18 which gives a measure of the extent to which the system deviates from the ideal.

Despite the evidence that results given by the dynamic method are high, this technique is preferable for routine determination of free base in GB for the following reasons:

(i) reproducibility is very good and much superior to that given by the static method. If therefore the same apparatus is used for relating partial pressure to mole fraction of base in pure GB and for examination of unknown samples, the error due to possible adsorption of vapour on the glass will be eliminated.

(ii) the procedure is much more convenient.

Measurements made on technical GB of high acidity are shown in Fig.4. It will be noted that the apparent acidity value gives little indication of the amount of triethylamine which would react with the acid impurities.

Results of similar measurements on samples of pure GB to which known amounts of acidic materials had been added are summarised in Appendix 2 and graphed in Figs. 5 and 6. The amounts of triethylamine reacted with iso-propyl hydrogen methylphosphonate ('half-ester') and with methyl phosphono-fluoridic acid ('fluoro acid') correspond fairly well with the formation of a 1:1 salt, the fluoro acid being the stronger as expected. The equilibrium constant (calculated on mole fractions and assuming the salt to be un-ionised) for the 'fluoro-acid' is approximately $9.3 \times 10^2$ compared with $2.8 \times 10^2$ for the 'half-ester'. Methyl phosphonic acid appears to be slightly stronger than the 'half-ester' and there is evidence of the second hydroxyl group co-ordinating slightly when triethylamine is present in excess. The curve for HF indicates that four moles of acid co-ordinate with three of base; this would not be inconsistent with the conductimetric results obtained by Wardrop and Bryant (7). The data for methyl phosphonic difluoride would correspond to the formation of $Et_3N.2\ MePOF_2$ and that for the dichloride appears to be similar but results both with $MePOCl_2$ and with isopropyl methyl-phosphonochloridate ('chloro GB') are suspect as trouble was experienced due to the precipitate clogging the capillary in the bubbler.

## Conclusions

A simple method of estimating free triethylamine in GB has been developed and has been used to measure the partial pressure of triethylamine over GB in low mole fractions. Some data on acid base equilibria in GB have also been obtained.

The marked positive deviations from ideality shown by the triethylamine/GB system are of interest from the practical viewpoint in that the volatility of the base will be considerably greater than would be expected from the vapour pressure of the pure material.

- 4 -

The implications of the data on acid-base equilibria can most readily be appreciated by considering the 'fluoro-acid' and 'half-ester' both of which are likely impurities which appear to form simple 1:1 salts with triethylamine. The approximate proportion of acid co-ordinated by varying amounts of amine are tabulated below:

| Et₃N added (Mole per cent of acid present) | Per cent of acid present co-ordinated with Et₃N | |
|---|---|---|
| | Fluoro Acid | Half Ester |
| 80 | 75 | 66 |
| 100 | 88 | 77 |
| 120 | 95 | 86 |

This emphasises the desirability of keeping the acidity of the GB low rather than relying too much on its 'neutralisation' by added base.

It would be of interest to extend this investigation to bases other than triethylamine.

Acknowledgements

Mrs. E. Lotts gave assistance with the experimental work. Mr. P.J. Bryant purified the GB.

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## Appendix 1 to P.T.P. 528

## Colorimetric Estimation of Triethylamine

Stock Solution. One gram of iodine (A.R.) in 100 ml. chloroform (A.R.) may be kept indefinitely in the dark with a well stoppered bottle. For use, 10 ml. of stock solution is diluted to 100 ml. with chloroform.

Procedure. To a suitable aliquot of the sample (in chloroform) in a 25 ml. flask add 5 ml. of the 0.1 per cent iodine solution. Place in a bath at 25°C for 10 min., then leave for 5 min. to reach room temperature before making up to 25 ml. with chloroform. Measure on the Spekker using 601 Filters and a blank solution in the reference cell.

Interference, from volatile acidic compounds such as HF and $MePOF_2$ was overcome by first shaking the sample with 0.1N. NaOH saturated with chloroform. A test estimation with chloroform containing a known amount of $Et_3N$ and $MePOF_2$ showed this procedure to give results which were correct to within five per cent.

## Appendix 2 to P.T.P. 528

## Acid-Base Equilibria in GB

1. Isopropyl hydrogen methyl phosphonate

| Wt. of GB (gm) | Wt. of Acid (gm) | Wt. of Et₃N (gm) | Mole Fractn. Acid | Mole Fractn. Et₃N | Concn. of Et₃N in air (mg/l) | Equivt. Mole Fr. Et₃N in liquid |
|---|---|---|---|---|---|---|
| 4.773 | 0.2710 | 0.1225 | 0.053 | 0.032 | 4.2 | 0.004 |
| 4.715 | 0.2652 | 0.1671 | 0.051 | 0.044 | 11.7 | 0.009 |
| 4.941 | 0.2618 | 0.3239 | 0.047 | 0.079 | 40.0 | 0.036 |
| 4.820 | 0.2643 | 0.4832 | 0.047 | 0.117 | 71.0 | 0.072 |

2. Methyl phosphonofluoridic acid

| | | | | | | |
|---|---|---|---|---|---|---|
| 4.720 | 0.2441 | 0.1851 | 0.066 | 0.048 | 3.2 | 0.0025 |
| 4.830 | 0.2562 | 0.2667 | 0.066 | 0.066 | 8.8 | 0.008 |
| 4.618 | 0.2307 | 0.3015 | 0.061 | 0.078 | 23.2 | 0.020 |
| 4.705 | 0.2410 | 0.4132 | 0.061 | 0.102 | 46.0 | 0.0425 |

3. Methyl phosphonic acid

| | | | | | | |
|---|---|---|---|---|---|---|
| 4.469 | 0.1059 | 0.1056 | 0.032 | 0.031 | 6.9 | 0.006 |
| 4.622 | 0.1095 | 0.2080 | 0.032 | 0.057 | 26.1 | 0.023 |
| 4.425 | 0.1048 | 0.3039 | 0.031 | 0.084 | 53.0 | 0.050 |

4. Hydrofluoric acid

| | | | | | | |
|---|---|---|---|---|---|---|
| 5.197 | 0.039 | 0.1080 | 0.049 | 0.027 | 9.5 | 0.0085 |
| 5.100 | 0.042 | 0.2262 | 0.052 | 0.055 | 22.0 | 0.019 |
| 5.442 | 0.040 | 0.3307 | 0.046 | 0.075 | 44.0 | 0.040 |
| 5.096 | 0.043 | 0.5092 | 0.049 | 0.116 | 83.0 | 0.080 |

5. Methyl phosphonic difluoride

| | | | | | | |
|---|---|---|---|---|---|---|
| 4.438 | 0.2098 | 0.1093 | 0.060 | 0.031 | 6.6 | 0.006 |
| 4.715 | 0.2240 | 0.2038 | 0.059 | 0.053 | 38.3 | 0.034 |
| 4.479 | 0.2695 | 0.3527 | 0.071 | 0.092 | 70.0 | 0.069 |
| 4.416 | 0.2224 | 0.3384 | 0.060 | 0.090 | 66.0 | 0.065 |

6. Isopropyl methylphosphonochloridate *

| | | | | | | |
|---|---|---|---|---|---|---|
| 5.841 | 0.1446 | 0.1104 | 0.017 | 0.025 | 12.7 | 0.011 |
| 5.364 | 0.1366 | 0.2084 | 0.021 | 0.050 | 39.0 | 0.035 |

7. Methyl phosphonic dichloride *

| | | | | | | |
|---|---|---|---|---|---|---|
| 4.645 | 0.2390 | 0.4150 | 0.046 | 0.106 | 82.0 | 0.080 |

* Precipitate formed.

- 8 -

FIG. I B. CIRCULATING PUMP.

MOTOR.

MERCURY.

ROCKER.

TO BUBBLER.

MERCURY.

TO GAS PIPETTE.

POLYTHENE TUBING.
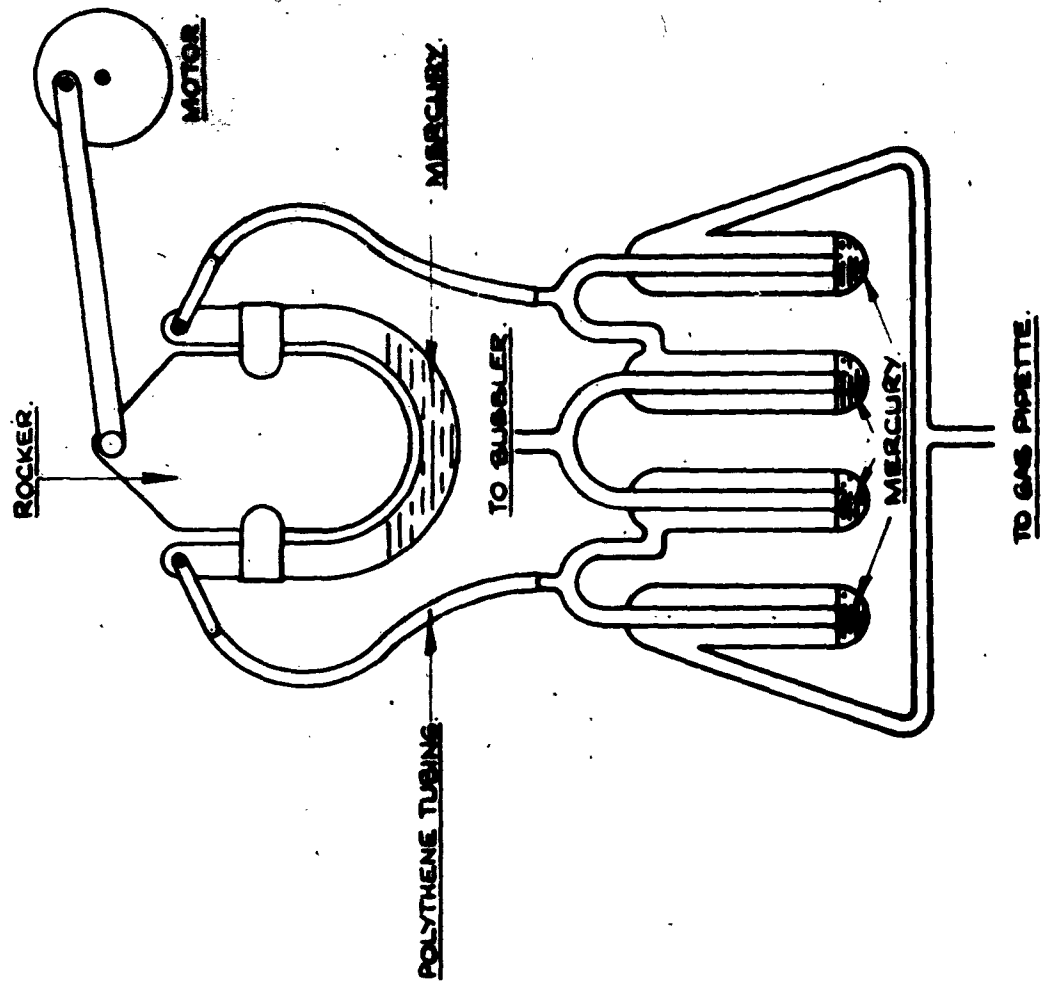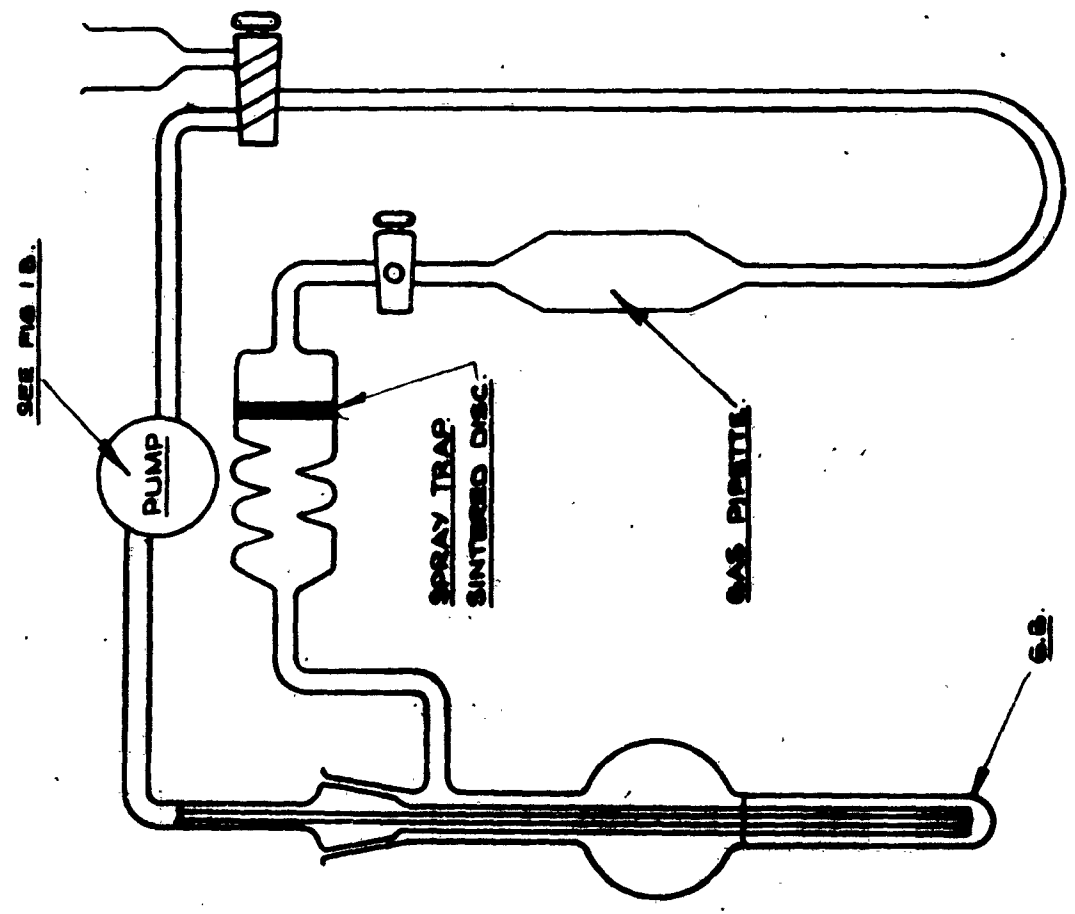
FIG. I A. PARTIAL PRESSURE APPARATUS — DYNAMIC.

SEE FIG. I B.

PUMP.

SPRAY TRAP
SINTERED DISC.

GAS PIPETTE.
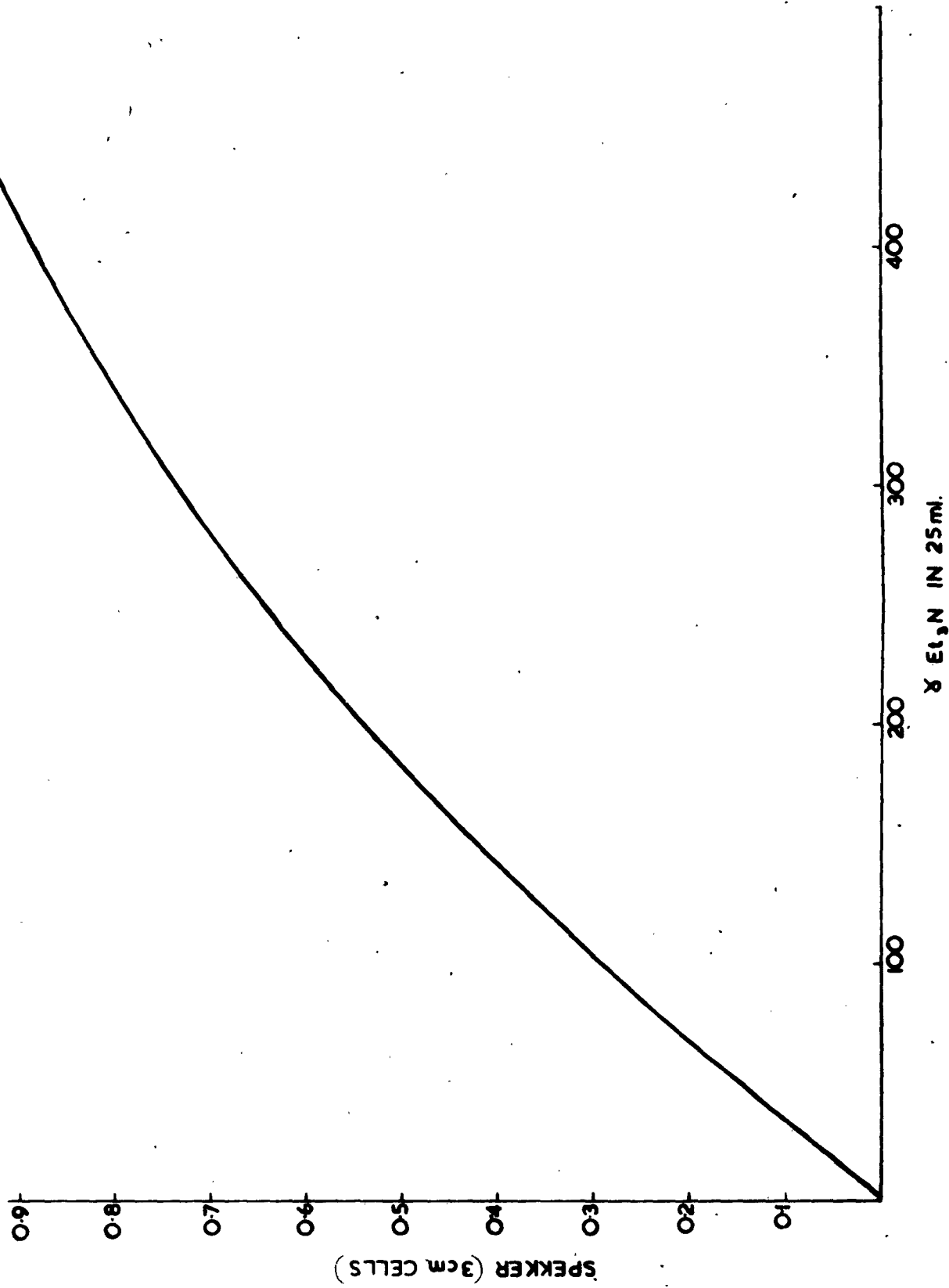
FIG.2    ESTIMATION OF Et₃N WITH IODINE: CALIBRATION CURVE

PORTON TECHNICAL PAPER 528

PT.2905

PARTIAL PRESSURE OF TRIETHYLAMINE OVER PURE GB (20°C)

① THEORETICAL (RAOULTS LAW.)

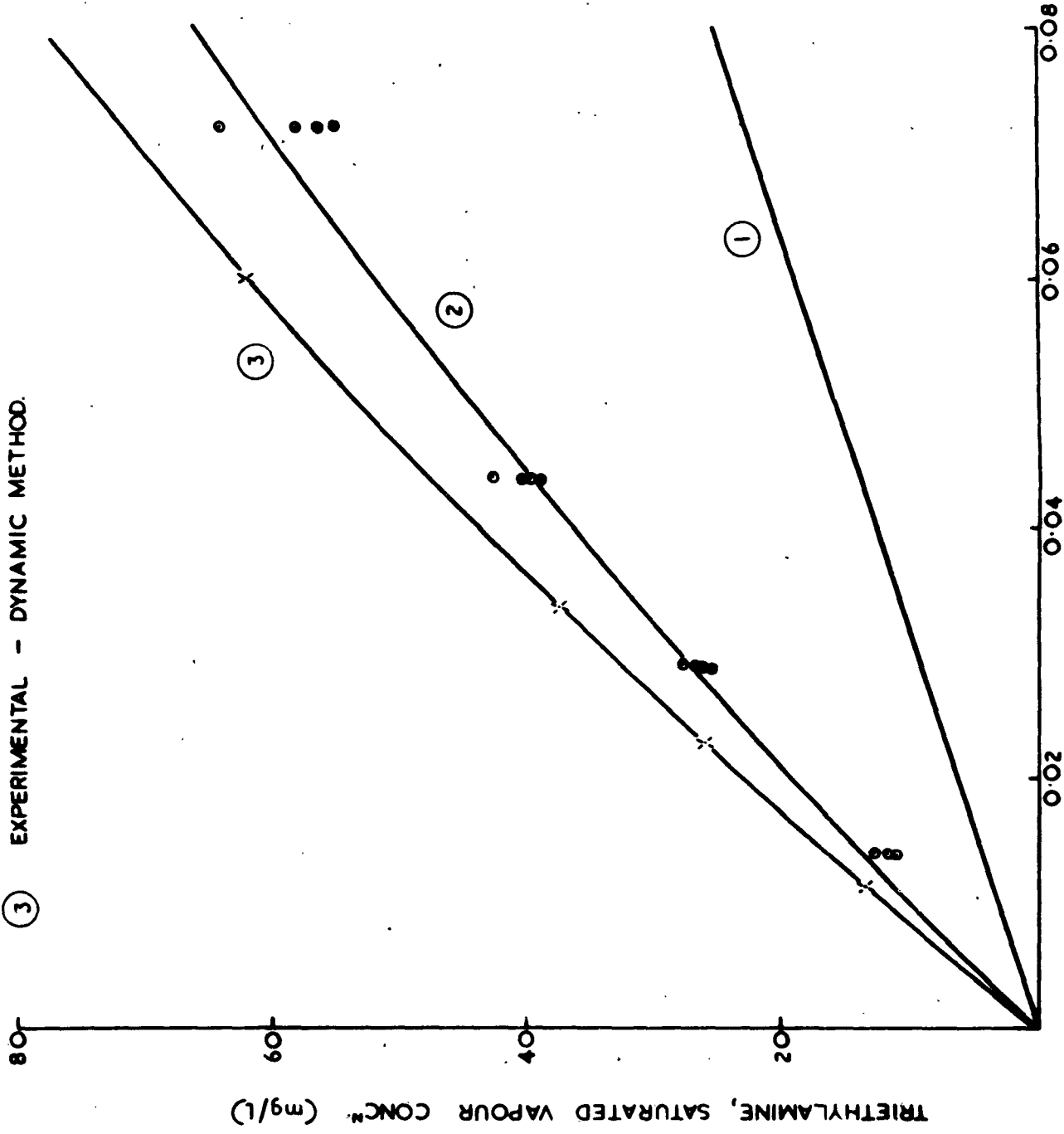② EXPERIMENTAL – STATIC METHOD.

③ EXPERIMENTAL – DYNAMIC METHOD.

TRIETHYLAMINE, SATURATED VAPOUR CONCⁿ (mg/l)

MOLE FRACTION OF TRIETHYLAMINE.

FIG. 3

TECHNICAL G.B. (ACIDITY 490 P.P.M)

MOLE FRACTION Et₃N ADDED

MOLE FRACTION Et₃N IN LIQUID AT EQUILIBRIUM
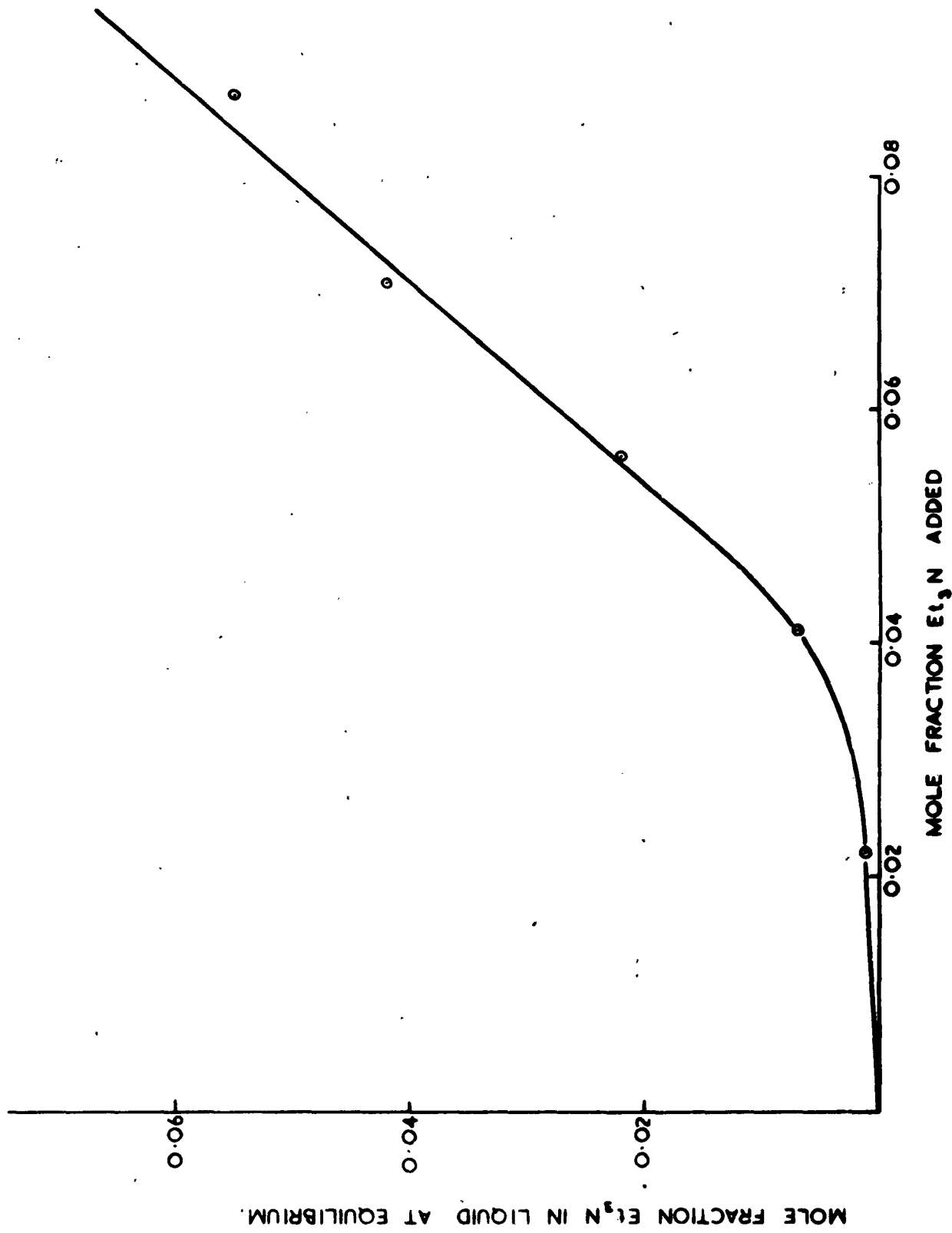
FIG. 4

FIG. 5    ACID-BASE EQUILIBRIA IN G.B.

① ISOPROPYL HYDROGENMETHYL PHOSPHONATE.

② METHYL PHOSPHONOFLUORIDIC ACID.

③ METHYL PHOSPHONIC ACID.

MOLES Et₃N ADDED PER. MOLE OF ACID PRESENT

MOLES FREE Et₃N IN LIQUID PER. MOLE ACID AT EQUILIBRIUM.

MOLES Et$_3$N ADDED PER MOLE OF ACID PRESENT

① HF

② Me POF$_2$

MOLES FREE Et$_3$N IN LIQUID PER MOLE ACID AT EQUILIBRIUM.
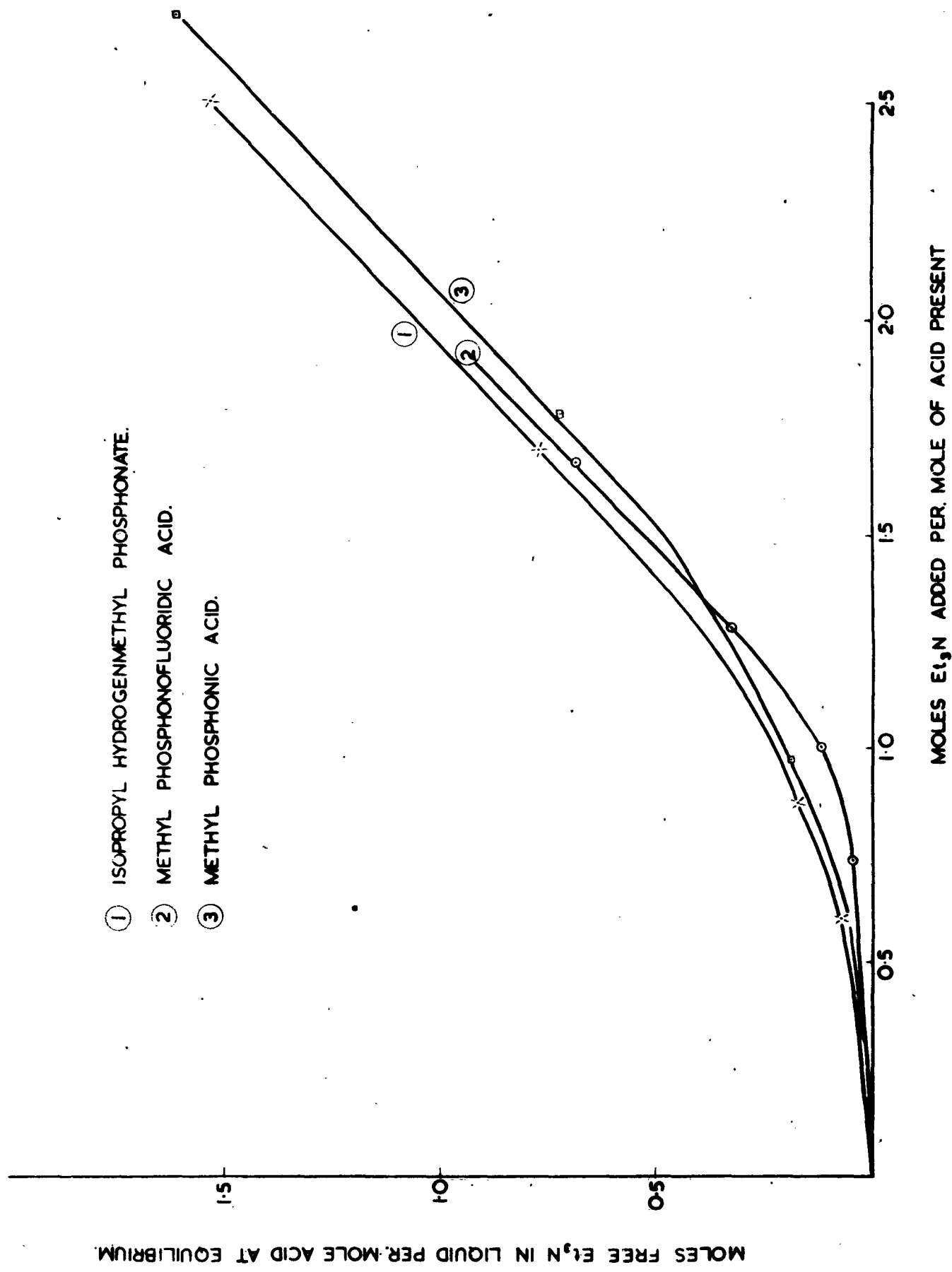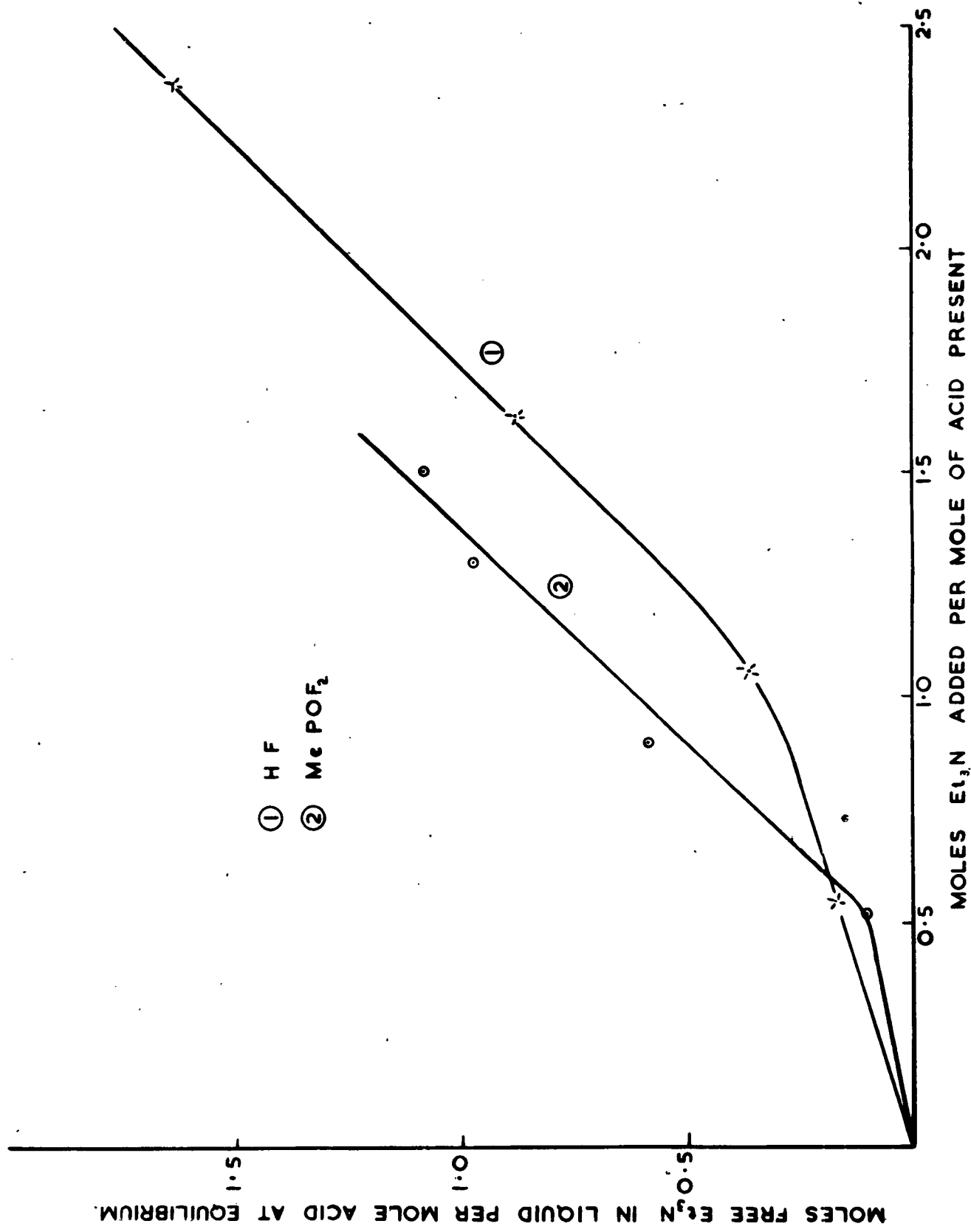
FIG 6. ACID—BASE EQUILIBRIA IN G.B.

P.T.P. 528

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